ICEI 2016

Singapore

International Conference on Electrified Interfaces

Contents

Welcome address

Dear colleagues and friends,

It is my distinct pleasure to welcome you all to the XIVth International Conference on Electrified Interfaces (ICEI). The ICEI belongs to the series of conferences started in 1979 with the title "Non-traditional Approaches to the Electrode/Electrolyte Interface", later modified into "Interdisciplinary Conference on Electrified Interfaces" and finally deviating to "International Conference on Electrified Interfaces". When I first joined the ICEI in 2004 (in Spa, Belgium), I was told that it was some kind of “triennial family meeting of non-traditional electrochemists”, which I think still holds today. As time went by, however, the term “non-traditional” slowly becomes redundant. The amendment of “pure” electrochemical methods by spectroscopy, imaging, or diffraction methods, and a close entangle¬ment with modern materials science has become state-of-the-art, and is flourishing. With my own background being to a large extent in Surface Science, I have actively tried to widen the family and include new members who are rather fresh with respect to activities at the solid-liquid interface.

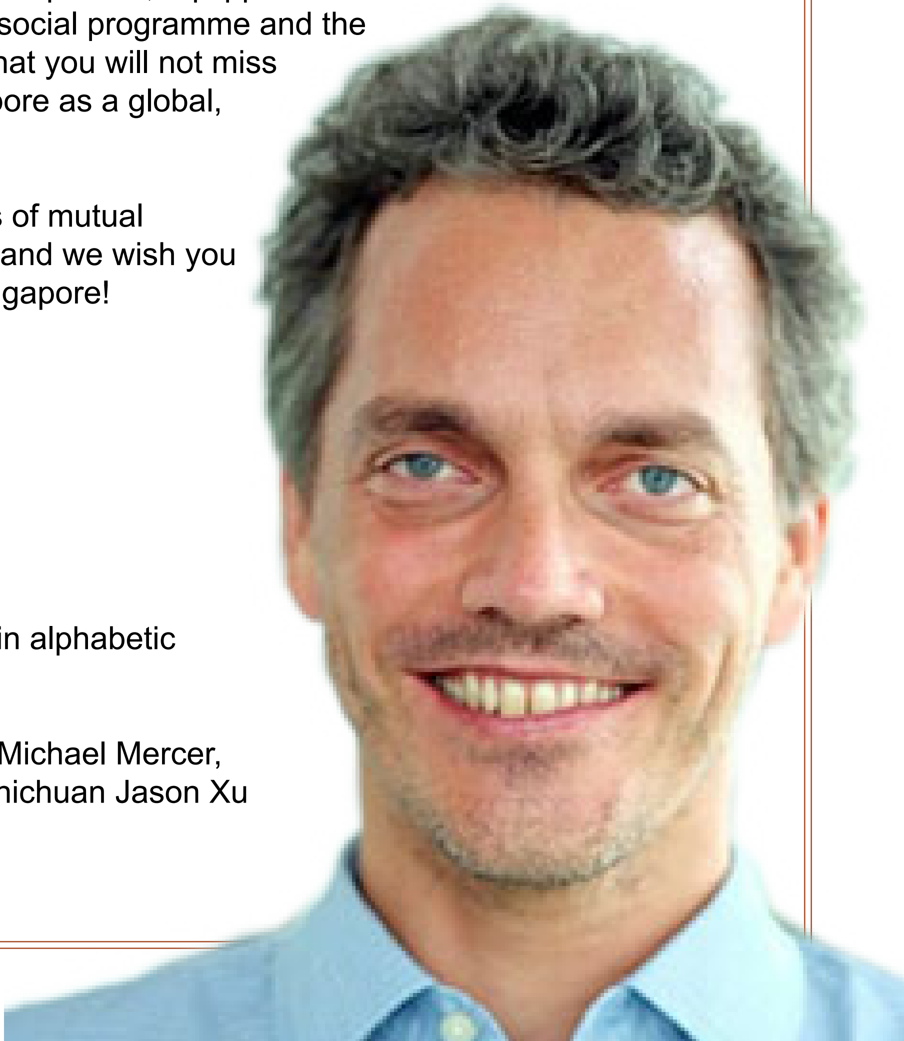
Another element central to the ICEI is the venue. Many important discussions happen in the breaks, over dinner, and over drinks. Most conference venues in Singapore are downtown, potentially resulting in the unexpected volatility of the participants. Imagine how happy we were when we discovered the cosy Changi Cove hotel: close to the solid-liquid interface (beach), close to the airport, yet surrounded by greenery; and, most important, equipped with excellent conference and accommodation facilities. Our social programme and the conference dinner will make sure that you will not miss the stunning impressions of Singapore as a global, intercultural high-tech metropolis.

We look forward to five fruitful days of mutual knowledge update and inspiration, and we wish you a good time at the ICEI 2016 in Singapore!

Harry Hoster,

on behalf of the Organising Team (in alphabetic order):

Craig Armstrong, Robyn Lockhart, Michael Mercer, Shahin Nikman, Kathryn Toghilll, Zhichuan Jason Xu



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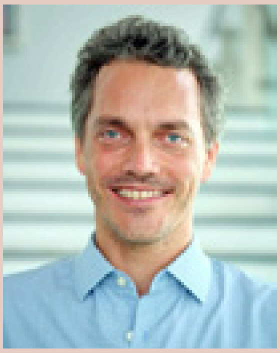

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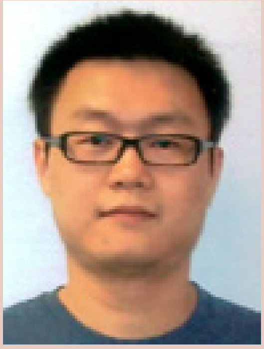

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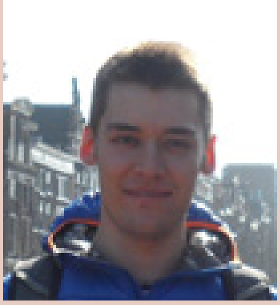

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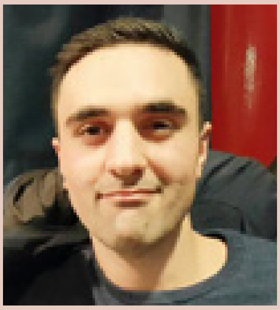

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Conference support

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Autolab/PGSTAT204 - small and powerful

The Autolab/PGSTAT204 is the smallest of the modular potentiostat/galvanostat instruments made by Metrohm Autolab. This instrument combines a small footprint with a modular design, allowing you to configure the Autolab instrument to fit your experimental requirements.

The instrument includes a base potentiostat/galvanostat with a compliance voltage of +/- 20 V and a maximum current of 400 mA. Combined with the Booster10A, the maximum current can be increased to +/- 10 A, making the instrument suitable for electrochemical measurements in a wide range of applications, from experiments on ultra-microelectrodes or sensors to high power fuel cells and batteries.

The instrument can be expanded with one additional internal module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module or the dual mode BA bipotentiostat module.

The Autolab/PGSTAT204 is a very affordable instrument which can be located anywhere in the lab. It comes with a built-in analog integrator as well as analog and digital interfacing options to combine it with external equipment.

Modular solutions

The Autolab/PGSTAT204 is compatible with a wide range of modules and accessories.

3 year
instrument warranty

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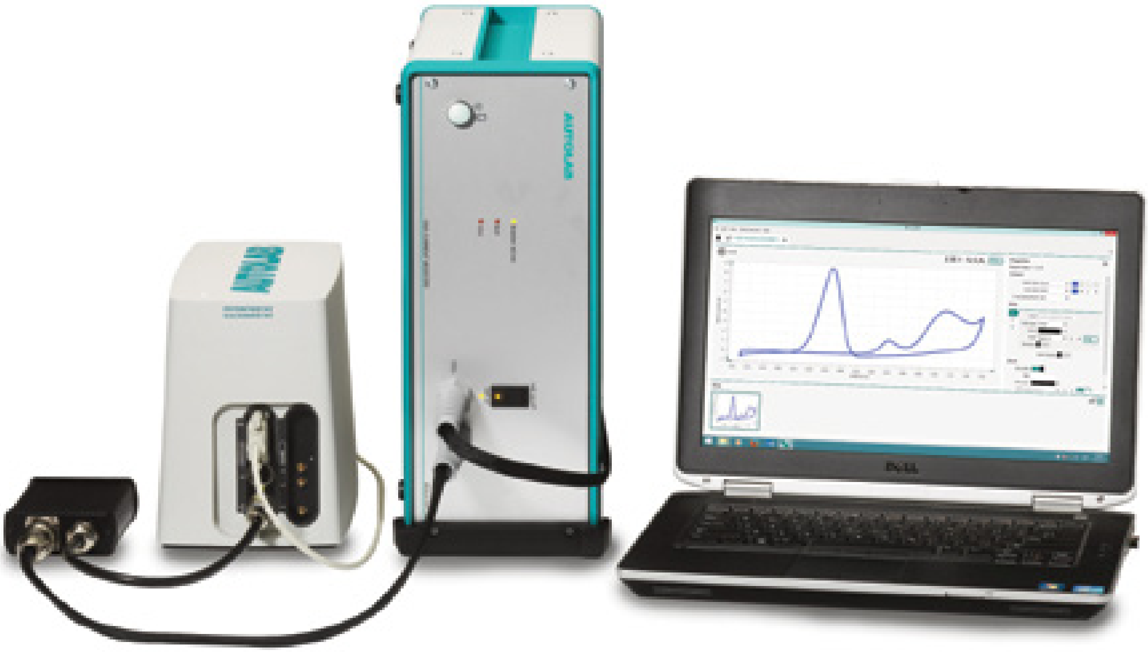
Optional modules

- Booster10A - 10 A booster for high current applications
- FRA32M - Module for electrochemical impedance spectroscopy
- BA - Module for bipotentiostatic measurements in combination with Autolab RRDE
- pX1000 - pH and temperature measurements module
- MUX - Multiplexer module for high-throughput electrochemical measurements
- EQCM - Electrochemical quartz crystal microbalance module
- IME663 - Interface for the Metrohm 663 VA Stand for electroanalytical measurements and trace analysis

Accessories

- Autolab RDE and RRDE - For measurements in hydrodynamic measurements
- Autolab LED Driver - For measurements on photovoltaic devices
- Autolab Electronic Load Interface - For connection to programmable load or powersupply

SPECIFICATIONS	Autolab/PGSTAT204	PGSTAT204 + Booster10A
• Electrode connections	2, 3 and 4	2, 3 and 4
• Potential range	+/- 10 V	+/- 10 V
• Compliance voltage	+/- 20 V	+/- 20 V
• Maximum current	+/- 400 mA	+/- 10 A
• Current ranges	100 mA to 10 nA, in 8 decades	10 A to 10 nA, in 9 decades
• Potential accuracy	+/- 0.2 %	+/- 0.2 %
• Potential resolution	3 uV	3 uV
• Current accuracy	+/- 0.2 %	+/- 0.2 %
• Current resolution	0.0003 % of current range	0.0003 % of current range
• Input impedance	> 100 GOhm	> 100 GOhm
• Potentiostat bandwidth	1 MHz	4 kHz
• Computer interface	USB	USB
• Control software	NOVA	NOVA



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Welcome to Changi Cove

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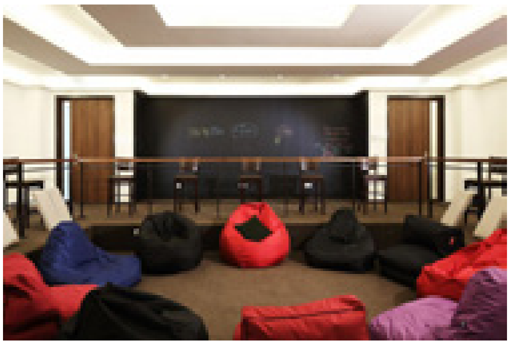
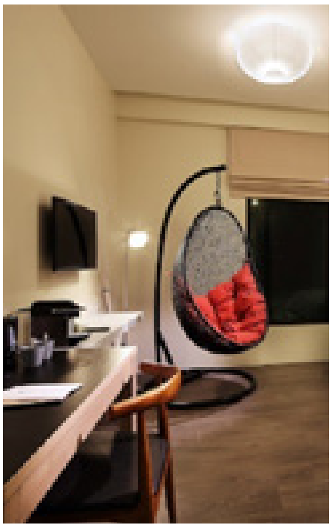
CHANGI COVE

The Changi Cove is situated in four hectares of lush greenery on the most north-eastern tip of Singapore and conveniently located next to the airport. To its north is the beautiful island of Pulau Ubin, which offers a peaceful and tranquil setting, untouched by urban development, concrete building and tarmac roads. Despite its seclusion, the centre is merely 26 Km from the busy city centre and 30-40 Km to world famous attractions such as the Singapore National Orchid Garden.

The Changi Cove itself is a modern establishment which provides a refreshing destination for retreats, meeting and events. Consisting of the GateWay conference centre, MyPlace Hotel and the CommandHouse, the Changi Cove boasts a wide range of facilities in order to make your stay comfortable, successful and memorable.



The Changi Cove has several different conference and function rooms to offer, which can accommodate small meetings or audiences upwards of 200 guests. The main room for Symposia is the 396 square meter auditorium, which has a seating capacity of 210, various audio and visual systems and a portable stage for presentations. The room is also retractable and can be turned into a 4000 square foot open space for banquets and functions. Beside the auditorium, the Changi Cove offers a total of 8 different meeting rooms and a unique 'Incubator' space which consists of many relaxed chairs and sofas which allow for big group meetings and team building activities.



Hotel Facilities

The hotel on-site includes a total of 112 comfortable guestrooms which are situated inside a restored heritage building. Its plentiful accommodation has been specifically designed to "promote rest, fresh perspectives, new ideas and bonding" and features a cosy and simplistic decor with specially painted walls, on which guests are encouraged to write, doodle or draw.

Monday Evening Concert

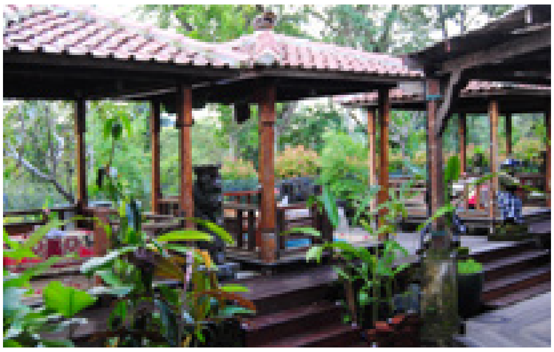
Drinks in the prefunction room at 5pm will be followed by a 45 minute concert 6-7pm before dinner.

Seyra is a band that enchants listeners with their own brand of dreamy indie folk-pop. The Singaporean multi-ethnic sextet blends emotional lyricism with layered guitar melodies, soaring hooks, and a distinctive, ethereal voice.

Thursday Evening Banquet

A banquet dinner will be held in Blue Bali. Transport depatures 7:45pm from Changi Cove. First return to hotel at 10:30pm. Second return at midnight.

Nestled on the edge of Singapore's iconic Botanic Gardens is a little piece of Bali. Blue Bali is an outdoor Balinese garden bar and restaurant backing on a charming colonial house (circa 1935). Comprised of a Bali-themed courtyard garden, traditional Javanese Joglos, Lesehans, daybeds and relaxing art deco furniture, a place to chill-out and relax.



Excursions

You are all travelling all this way to heart of Asia, so a taste of Singapore is a must! We have organised three excursion options, hopefully something to suit everyone. Below each excursion is outline, along with the associated small fee to cover the transport costs. Do note, there will be limited numbers on each excursion, so do express interest and sign up as soon as you know which one inspires you the most!

For excursion 1A, we will be taking payment at the conference venue and then walk to the ferry terminal. Excursion 1A will not run in the event of poor weather – there is a separate excursion (1B) that will run if this is the case. For excursions 2 and 3, there is a combined total sign-up of 40 and this will be decided on a first come, first serve basis. For these excursions, please announce on the coach which of the two excursions you are going on and make your payment. Please remember to bring enough Singapore dollars with you to cover the trip! We have appointed one person from our team to lead each excursion on the day. Note that our mobile numbers may be subject to change once we are in Singapore; please check at registration:

Excursion 1A/1B:
Prof. Harry Hoster,
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Excursion 2:
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(+44) 7828 421830,
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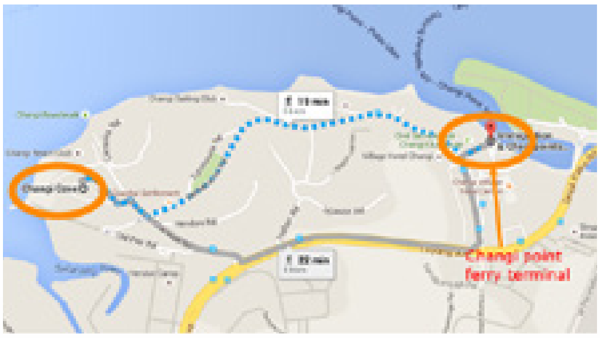
Excursion 2:
Dr. Michael Mercer,
(+65) 93612678,
m.mercer1@lancaster.ac.uk

1A Pulau Ubin

The excursion will begin with a picturesque walk along the coast to the ferry terminal. Take a scenic ferry ride to the luscious island of Pulau Ubin. On arrival, we will enjoy the views on the island by mountain bike, taking a trip to the Chek Jawa Wetlands, one of Singapore's richest ecosystems. Here you are free to enjoy the views from the 1 kilometre boardwalk or Jejawi Tower. Before the return ferry journey there will be the chance to explore the shops and eateries on the island.

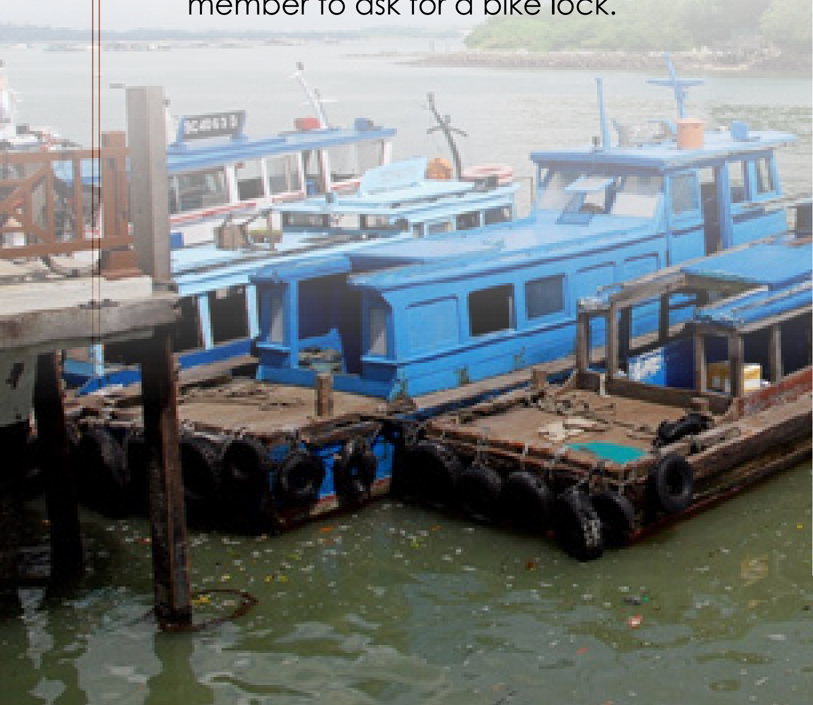
Total Cost per person: $20
including the ferry crossing and bike rental.



14.30: Depart from Changi Cove; walk to ferry terminal.
15.00: ETA at Changi point ferry terminal. Ferry journey ~20 minutes, each boat takes up to 12 people at a time.
15.45: ETA of all passengers at Pulau Ubin. Bicycle hire ~$10 SD for a good bike. Remember to ask for a bike lock.

16.15: ETA of passengers at Chek Jawa. Secure bikes.
N.B. for the more adventurous among you, there is also the option of a mountain bike trail. A map is provided but the main group will go to Chek Jawa.

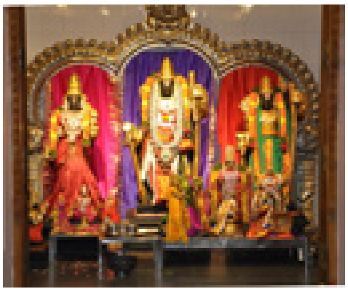
16.30-17.45: Leisure time at Chek Jawa Visitor centre. Highlights include: Jejawi tower, walks along boardwalk to view wildlife, self-guided tours.
18.00: Rendezvous at location where bikes are secured.
18.30: ETA at meeting point for ferry departure.
19.15: ETA back and Changi Point and walk back to hotel.
Note: if the trip is not feasible due to poor weather, we will instead visit the Changi Chapel museum and the Sri Ramar temple. This is described as excursion 1B.



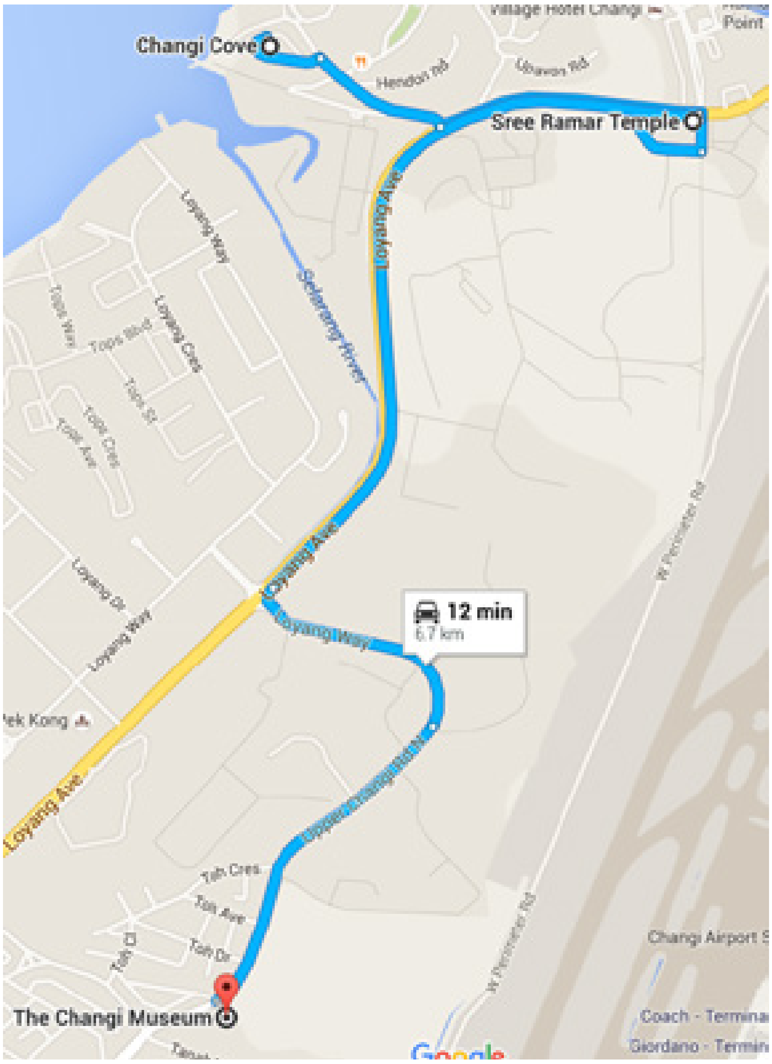
1B Changi Chapel museum and Sree Ramar temple

Please note, we will only be running this excursion in the event that poor weather prevents excursion 1A (Pulau Ubin) from taking place. In this eventuality, taxis will be provided. Depending on interest, we will charge just enough to cover the cost of the taxis.

The Changi Chapel museum is dedicated to those in Singapore who lived and died through World War II, providing insight in the events that unfolded during the Japanese Occupation.

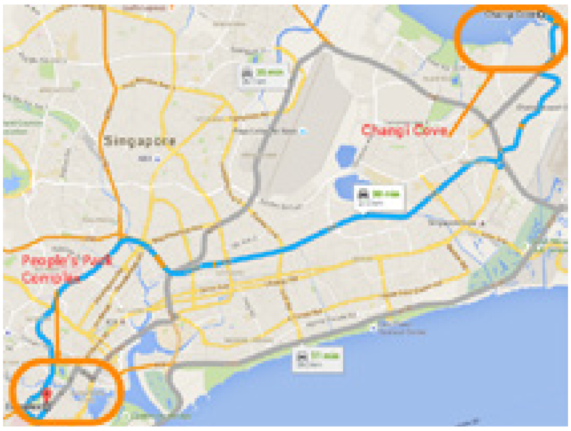


The Sree Ramar temple is dedicated to the Hindu god Rama



2 Chinatown

Embrace the hustle and bustle of the historic Chinatown area. We will explore the Buddha Tooth Relic Temple and Museum. Please note, out of respect for the temple, please come in appropriate attire (*no bare backs, shorts or mini-skirts*). For those of you who enjoy shopping, there will be plentiful opportunities to explore the markets. Not to mention ample photographic opportunities of breath-taking Chinese, but also Hindu, temples and mosques.



Total Cost per person: $20
including travel to and from Downtown Singapore.

14.30: Coach to depart from Changi Cove
15.15: ETA at People's Park Complex, Chinatown
15.30 - 16.45: Free time to explore the Buddha Tooth Relic Temple
16.45: Meet in Temple foyer. Walk outside Sri Mariamman Temple on Temple Street and everyone to explore at their leisure
17.00-19.00: Exploration of markets and remaining temples.
19.00: Rendevous at People's Park Complex
19.30: Coach departure from People's Park Complex.

3 Marina Bay Sands and Gardens

We will visit the rooftop of the Marina Bay Sands Hotel (Sands Skypark), to enjoy the stunning views of Singapore, and the eclectic restaurants and bars. We will also be visiting the nearby Gardens by the Bay, a 101 hectare nature park. This will include a chance to visit various attractions, including the OCBC skyway, and various conservatories including Flower Dome and Cloud Forest.

Total Cost per person: $50 including entry to the Sands Skypark, the OCBC Skyway and travel

Itinerary

14.30: Coach to depart from Changi Cove
15.30: ETA outside Marina Bay Sands Hotel, after stop-off in Chinatown
15.30-17.00: Purchase tickets for Sands Skypark Observation Deck from Box offices, free time to enjoy the views from the roof, visit bars etc.
17.00-17.15: Walk to Gardens by the Bay via Lions Bridge. To purchase tickets for the
17.15-18.15: Free time to explore Gardens by the Bay
18.30: Meet up at the "i" meeting point shown on the map.
18.30-19.15: OCBC Skyway
19.15: Meet back by "i" by this time
19.15-19.45: walk back to Marina Bay Sands via Lions bridge to get on 19.45 coach.

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Digital Edition only:
* Link to Singapore Facts, Culture, Cuisine and phrases*

by Craig Armstrong

Singapore Emergency Telephone Numbers

Police, fire and ambulance services: who to call and what to say in an emergency or non-emergency situation...

Service	**Phone Number**
Police	**999**
Fire & Ambulance	**995**
Non-Emergency Ambulance	**1777**
Police Hotline	**1800 255 0000 (non-emergencies)**
Traffic Police	**6547 0000**

Call 999 only in an emergency. Do the following:

- Give a clear description of the nature of the emergency
- Give your name, telephone number and the location of the emergency
- Stay on the phone; do not hang up

The police guarantee to answer a 999 call within 10 seconds and in urgent cases be on the scene within 15 minutes. For non-emergency matters, use the police hotline or contact the relevant Neighbourhood Police Centre.
When using an international mobile telephone with a roaming provider dial 112 (GSM phone) or 911 to be redirected to the 999 emergency number.
The Singapore Civil Defence Force (SCDF) is responsible for emergency ambulance services, which will take the patient to the nearest public ("restructured") hospital. For non-emergency medical situations, call 1777 for a private ambulance. Calling 995 in non-emergencies will result in a fine.

Program - Monday

	opening
09:30	Session 1 In-situ Spectroscopy
10:00	
10:30	
11:00	COFFEE
11:30	Session 1 In-situ spectroscopy
12:00	
12:30	LUNCH
13:00	
13:30	
14:00	Session 2 Atomic Scale Imaging and Diffraction
14:30	
15:00	
15:30	COFFEE
16:00	Session 2 Atomic Scale Imaging and Diffraction
16:30	
17:00	DRINKS
17:30	
18:00	CONCERT
18:30	
19:00	DINNER
19:30	
20:00	
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21:00	
21:30	
22:00	

Program - Tuesday

09:00	
09:30	Session 3 Fundamentals of Electrocatalysis
10:00	
10:30	
11:00	COFFEE
11:30	Session 3 cont. Fundamentals of Electrocatalysis
12:00	
12:30	
13:00	LUNCH
13:30	
14:00	
14:30	Session 4 Applied Electrochemistry
15:00	
15:30	
16:00	
	COFFEE
16:30	Poster Mini-talks
17:00	
17:30	
18:00	DINNER
18:30	
19:00	
19:30	
20:00	Session 5 Poster Session
20:30	
21:00	
21:30	
22:00	

Program - Wednesday

09:00	
09:30	**Session 6** **Electrocatalysis Towards OER and ORR**
10:00	
10:30	
11:00	**COFFEE**
11:30	**Session 6 cont.** **Electrocatalysis Towards OER and ORR**
12:00	
12:30	
13:00	**LUNCH**
13:30	
14:00	
14:30	**Excursions**
15:00	
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Program - Thursday

09:00	
09:30	**Session 7** **New Electrocatalytic Materials**
10:00	
10:30	
11:00	**COFFEE**
11:30	**Session 7 cont.** **New Electrocatalytic Materials**
12:00	
12:30	
13:00	**LUNCH**
13:30	
14:00	
14:30	**Session 8** **Fundamentals Electrochemistry**
15:00	
15:30	
16:00	**COFFEE**
16:30	**Session 8 cont.** **Fundamental Electrochemistry**
17:00	
17:30	
18:00	
18:30	**BANQUET DINNER**
19:00	
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22:00	

Program - Friday

09:00	
09:30	**Session 9** **Nanostructures and Nanomaterials**
10:00	
10:30	
11:00	**COFFEE**
11:30	**Session 10** **Batteries**
12:00	
12:30	
13:00	Closing Remarks
13:30	**LUNCH**
14:00	
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1 In-situ Spectroscopy

T01

In-situ IR, XAS and ESMS-based studies of electrically polarized nickel, copper and gold electrode systems with pseudohalide ions in neat DMF and DMSO electrolytes

Michael R. Mucalo

T02

In-situ XPS apparatus for electrochemical reactions at solid/liquid interfaces

Takuya Masuda

T03

In-situ XPS studies of Ir stabilization effect in $IR_xRu_{1-x}O_2$ electrocatalysis during the oxygen evolution reaction

Viktoriia A. Saveleva

T04

Probing oxygen and hydrogen evolution reactions using in-situ raman spectroscopy

Jason Boon Siang Yeo

T05

In-situ ATR-FTIR analysis of methylated amorphous silicon as negative electrode material for Li-ion batteries

Bon-Min Koo

T06

In-situ Raman spectroscopic study on the electrochemical oxidation of Pt(111) and Pt(100) single crystals

Yi-Fan Huang

Chairs: Prof. Zhichuan Xu and Prof. Katsuyoshi Ikeda

T01

In situ IR, XAS and ESMS-based studies of electrically polarized nickel, copper and gold electrode systems with pseudohalide ions in neat DMF and DMSO electrolytes

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Summaries [1-3] are provided of subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS), X-ray absorption (XAS) and Electrospray mass spectrometry (ESMS) studies probing the electrochemistry of “pseudohalide ions”, i.e. cyanide/cyanate/thiocyanate/selenocyanate and tellurocyanate ions with electrically polarized nickel, copper and gold electrodes in neat dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) electrolytes. Applied potential varied from -1500 mV to +2000 mV(AgCl/Ag). Cyano-based species in the electrolytes allowed detection of electrogenerated products from 2400-1900 cm^{-1} where few other IR fundamentals occur.

In general, the SNIFTIRS/potentiometric studies indicated:
1) solvent adsorption
2) electrodissolution of the metal electrodes to form metal/pseudohalide species
3) insoluble film formation/passivation
4) gas evolution
5) decomposition of (TeCN$^-$)
6) electrocatalytic processes

X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption fine structure (EXAFS) elucidated the coordination geometry of the Ni-isocyanato, isothiocyanato and isoselenocyanato complex ions identified by SNIFTIRS investigations in the DMSO-based electrolytes. XANES also showed the importance of the Cu(I) species in DMSO electrolytes. SNIFTIRS studies of the TeCN$^-$ ion with Ni, Cu and Au electrodes were the first of their kind, showing decomposition of TeCN$^-$ to form deposited Te and free CN$^-$ leading to metal-cyano complex ions being formed. The sensitivity (to decomposition) of the TeCN$^-$ ion by polarizing cations was seen as a potentially promising sensor for detecting cation species forming on the electrode.

References:

[1] An X-ray absorption spectroscopy investigation of the coordination environment of electrogenerated Ni(II)-pseudohalide complexes arising from the anodic polarization of Ni electrodes in DMSO solutions of NCO-, NCS- and NCSe- ions, Alwis, Kethsiri H. K. L.; Ingham, Bridget; Mucalo, Michael R.; Kappen, Peter; Glover, Chris, RSC Advances 5(20) (2015),15709-15718.

[2] In situ IR study of the anodic polarization of gold electrodes in polar aprotic solvents: DMSO and DMF solutions of cyanate, thiocyanate and selenocyanate ions, Alwis, Kethsiri H. K. L.; Mucalo, Michael R., J. Electrochem. Soc. 161(12), (2014), H738-H750.

[3] A fundamental in situ IR spectroelectrochemical study of the electrical polarization of nickel, copper and gold electrodes in the presence of the unstable tellurocyanate ion in DMSO and DMF solutions, Alwis, Kethsiri H. K. L.; Mucalo, Michael R.; Lane, Joseph R., RSC Advances 5(40), (2015), 31815-31825 (and other references).

T02

In situ XPS Apparatus for Electrochemical Reactions at Solid/liquid Interfaces

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X-ray photoelectron spectroscopy (XPS) is a powerful technique for the determination of surface compositions, oxidation states and electronic structures. Since XPS requires vacuum, it is a challenge to perform in situ XPS measurements at solid/liquid interfaces under electrochemical potential control. From the 1970s, “electrochemical-XPS”, where electrochemically-treated samples can be transferred into a vacuum chamber for XPS analysis without being exposed to open air, has been utilized for various systems including electrocatalysts for fuel cells [1]. Recently, in situ electrochemical XPS measurements in the presence of a thin liquid layer have been performed using room temperature ionic liquids [2] or near ambient pressure XPS apparatus with a differentially pumped electrostatic lens [3,4]. Although their results are important, these techniques cannot be utilized for electrochemical reactions in a sufficiently thick solution layer.

Here, we constructed an in situ XPS apparatus for electrochemical reactions at solid/liquid interfaces using a micro-volume cell equipped with an ultrathin photoelectron window [5,6,7]. In this system, the cell filled with an electrolyte solution is placed in a vacuum chamber for XPS analysis, x-rays are irradiated to the vacuum side of the window, and photoelectrons generated at the solid (window)/liquid (electrolyte solution) interface are detected through the window. Thus, electrochemical reactions in contact with a variety of “ordinary liquids” with a sufficient thickness can be performed.

Electrochemical growth of Si oxide in contact with water was observed as a first demonstration of the capability of this system. Effect of potential and time on the thickness of Si and Si oxide layers was quantitatively determined at sub-nanometer resolution [6].

References

[1] A. Wieckowski, J. K. Nørskov, Fuel Cell Science, John Wiley & Sons, Inc., Hoboken, New Jersey, 2010.
[2] K. R. J. Lovelock, et al., Chem. Rev. 2010, 110, 5158.
[3] M. Salmeron, R. Schlögl, Surf. Sci. Rep. 2008, 63, 169.
[4] O. Karslıoğlu, et al., Faraday Discussions, 2015, 180, 35.
[5] A. Kolmakov, et al., Nat. Nanotechnol. 2011, 6, 651.
[6] T. Masuda, et al., Appl. Phys. Lett. 2013, 103, 111605.
[7] J. J. Velasco-Velez, et al., Angew. Chem. Int. Ed., 2015, 54, 14554.

T03

In-situ XPS studies of Ir stabilization effect in $Ir_xRu_{1-x}O_2$ electrocatalysts during the oxygen evolution reaction

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Due to the higher stability of $Ir_xRu_{1-x}O_2$ electrocatalysts, in comparison to pure RuO_2, they have attracted much attention in recent years as prospective candidates for the oxygen evolution anodes in proton exchange membrane (PEM) water electrolysis cells [1]. Their catalytic properties and degradation/stabilization mechanism have been investigated using a variety of electrochemical as well as ex-situ surface analysis techniques [2-4]. However the mechanism of the stabilization effect, which Ir exerts on the Ru oxide, is not fully understood yet. In the present study we have applied synchrotron-radiation-based near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) [5] combined with an electrochemical cell, to provide in-situ information on the state of the $Ir_xRu_{1-x}O_2$/PEM interface during the oxygen evolution reaction (OER) with the aim to unveil the iridium impact on the mixed IrRu oxide degradation. Single RuO_2 and IrO_2 and mixed $Ir_{70}Ru_{30}O_2$ oxides were integrated into the PEM-based (Aquivion) membrane electrode assemblies. The XP spectra of the electrolyte and electrode components were obtained under 3 mbar water vapor pressure and at different electrode potentials. The oxygen evolution was confirmed by on line mass spectrometry. The data analysis revealed the presence of Ir and Ru in various oxidation states with fractions as well as Ir/Ru atomic ratio showing strong potential dependence. The formation of the volatile and soluble RuO_4 corrosion product was observed at potentials before the OER onset both for single Ru and mixed IrRu oxides. The conversion of a stable RuO_2 component to a less stable hydrous $RuO_2 \cdot xH_2O$ was found to be limited by the presence of iridium, whereas the iridium oxide itself did not undergo any redox changes under polarization.

The authors are indebted to M. Hävecker and A. Knop-Gericke from the FHI (Berlin) for the opportunity to use ISISS beamline (BESSY II) and HZB (Berlin) for the allocation of synchrotron radiation beamtime. The work was funded by the European Union's Seventh Framework Programme (FP7/2007-2013) for Fuel Cell and Hydrogen Joint Technology Initiative under Grant No. 621237 (INSIDE).

References

[1] Fabbri E, Habereder A, Waltar K, Kötz ER, Schmidt TJ Catal Sci Technol 4 (2014) 3800-3821.
[2] Kötz ER, Stucki S. Electrochim Acta. 31 (1986) 1311-1316.
[3] Kodintsev IM, Trasatti S., Rubel M, Wieckowski A, Kaufher N Langmuir 8 (1992) 283-290.
[4] Lyons MEG, Floquet S Phys Chem Chem Phys 13 (2011) 5314-5355.
[5] Knop-Gericke A, Kleimenov E, Hävecker M et al Adv Catal 52 (2009) 213-272.

T04

Probing Oxygen and Hydrogen Evolution Reactions Using In Situ Raman Spectroscopy

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We present two studies using primarily in situ Raman spectroscopy to understand the compositional changes of catalysts during electrochemical H_2 and O_2 evolution reactions.

We investigate first the electrochemical oxygen evolution reaction (OER) occurring on Cu, Cu_2O, $Cu(OH)_2$ and CuO catalysts in aqueous KOH electrolyte. All four catalysts were oxidized or converted to CuO and $Cu(OH)_2$ during the slow anodic sweep of cyclic voltammetry and exhibited similar activities for the OER. A Raman peak at 603 cm^{-1} appeared for all the four samples at OER-relevant potentials, >1.62 V vs. RHE. This peak was identified as the Cu-O stretching vibration band of a Cu^{III} oxide, a metastable species whose existence depends on the applied potential. Since this frequency matches well with that from a $NaCu^{III}O_2$ standard, we propose that the chemical composition of the Cu^{III} oxide is CuO_2^--like. The four catalysts, in contrast, did not oxidize the same way during direct chronoamperometry measurements at 1.7 V vs. RHE. Cu^{III} oxide was observed only on the CuO and $Cu(OH)_2$ electrodes. Interestingly, these two electrodes catalyzed OER approximately 10× more efficiently than the Cu and Cu_2O catalysts. By correlating the intensity of the Raman band of Cu^{III} oxide and the extent of the OER activity, we propose that Cu^{III} oxide is an active catalytic species for the electrochemical water oxidation. The formation of Cu^{III} oxides on CuO films during OER was also corroborated by in-situ XANES measurements of the Cu K-edge.

In-situ Raman spectroscopy was also used to study the hydrogen evolution reaction (HER) occurring on electrodeposited MoS_x films. A Raman peak which could be assigned to the S-H stretching vibration was identified during HER. Hence, we could directly establish that sulfur atoms are the catalytic active sites in amorphous MoS_x for proton reduction.

References

[1] Deng YL, Handoko AD, Du YH, Xi SB, Yeo BS. ACS Catal. In Press. 2016.

T05

In situ ATR-FTIR analysis of methylated amorphous silicon as negative electrode material for Li-ion batteries

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Silicon is an up-and-coming negative electrode material for Li-ion batteries with a high theoretical specific capacity (4200mAh/g at $Li_{4.4}Si$). However, stresses induced during repeated charging and discharging process yield to rapid capacity fade. We recently showed that a homogeneous amorphous silicon/carbon alloy, in which carbon is inserted as methyl groups ($a\text{-}Si_{1-x}(CH_3)_x{:}H$), has an improved cyclability, related to its mechanical softening by incorporation of CH3 groups.[1]

On the other hand, Li-ion batteries operate in a wide voltage window. The most known organic solvents are unstable across this voltage range and Solid Electrolyte Interphase (SEI) resulting from the reduction of inorganic and organic products is formed on negatively polarized anode during the 1st cycle. The formation of SEI leads to irreversible charge loss and its evolution over cycles is closely linked to the battery lifetime. [2]

In this study, we focus on SEI evolution upon cycling of methylated amorphous silicon deposited by Plasma Enhanced Vapor Chemical Deposition (PECVD) with several carbon contents (0, 5, and 10%). Thin films were deposited on a conductive, moderately doped silicon crystal used as an IR window for Attenuated Total Reflection Fourier Transform InfraRed spectroscopy (ATR-FTIR). It allows for obtaining in situ qualitative and quantitative information on the semiconductor/electrolyte interface with enhanced sensitivity. [3]

In this way, the composition and thickness of the SEI were followed during electrochemical lithiation/delithiation. It was found that introduction of methyl groups in the active material has a significant impact on the SEI formation and increases the SEI stability.

References

[1] L. Touahir, A. Cheriet, D. Alves Dalla Corte, J.-N. Chazalviel, C. Henry de Villeneuve, F. Ozanam, I. Solomon, A. Keffous, N. Gabouze, and M. Rosso, J. Power Sources, 240 (2013), 551–557.

[2] P. Verma, P. Maire, P. Novák, Electrochimica Acta 55 (2010) 6332–6341

[3] D. Alves Dalla Corte, G. Caillon, C. Jordy, J.-N. Chazalviel, M. Rosso, F. Ozanam, Adv. Energy Mater. (2016), 6, 1501768

T06

In-situ Raman spectroscopic study on the electrochemical oxidation of Pt(111) and Pt(100) single crystals

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Towards a fundamental understanding of the reactivity of the oxygen reduction reaction and the degradation mechanism of Pt catalysts, we employed in-situ shell-isolated nanoparticles-enhanced Raman spectroscopy to identify the intermediate stages of the electrochemical oxidation of Pt(111) and Pt(100) single crystal at the molecular level. In order to assign the experimental spectra to the surface species, the vibrational frequency of possible surface species were predicted by DFT calculation.

Figure 1 a and b show the cyclic voltammogram of Pt(111) and the in-situ potential-dependent Raman spectra of Pt(111) covered by silica coated-Au nanoparticles in 0.1 mol/L HClO4 electrolyte, respectively. Generally, it can be found that the voltammogram and the observed spectral features shows good correspondence. Specifically, at the potential negative to 1.0 V, the spectra show a characteristic band at 920~930 cm-1, which is assigned to the perchlorate anion in the double layer. At the potentials 1.0 V ~ 1.1 V, three bands at at 240 cm-1, 956 cm-1 and 1169 cm-1 appears, which are assigned to surface (su)peroxide. At the potentials above 1.3V, the band at 593 cm-1 appears and grows during the positive shift of potential, which is assigned to the bulk Pt oxide.

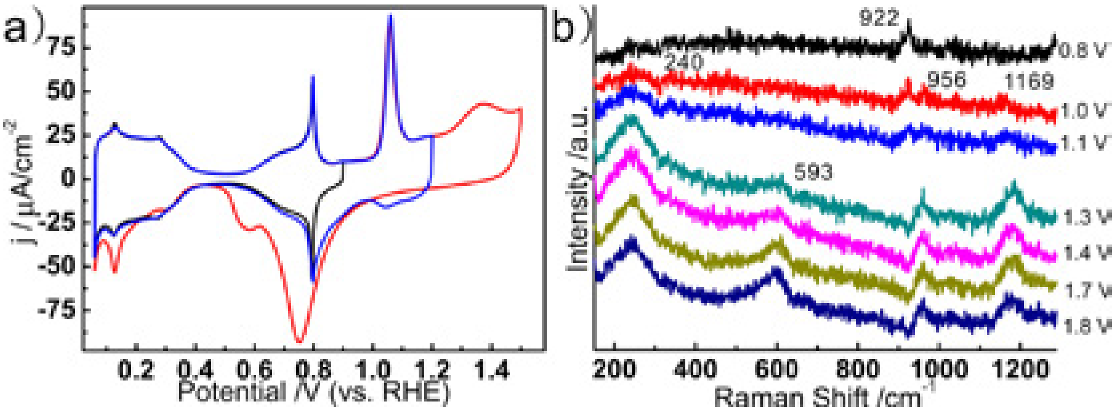

Figure 1. a) Cyclic voltammogram of Pt(111); b) Potential dependent Raman spectra of Pt(111) covered by Au@SiO2 nanoparticles in 0.1 mol/L HClO4;

References

[1] Huang YF, Kooyman P, Koper M. Nat. Commun. accepted.

2

Atomic Scale Imaging and Diffraction

T07	Ultrahihg resolution scanning probe microscopy on its way from vacuum to ambient and liquid environments *Franz J. Giessbl*
T08	Transmission surface diffraction: a novel method for operando studies of electrochemical interfaces *Olaf M. Magnussen*
T09	Ohmic microscopy: Further developments and future prospects *Daniel A. Scherson*
T10	Dealloying in 2D: Role of the local atomic environment *Philippe Allongue*
T11	A clockwork lotus: Electrochemical switching of boron nitride nanomesh wetting *Stijn F. L. Mertens*

Chairs: Prof. Harry Hoster and Prof Axel Groß

T07

Ultrahigh resolution scanning probe microscopy on its way from vacuum to ambient and liquid environments

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Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are powerful tools that enable high resolution studies of surfaces. In the past, STM and AFM were separate techniques that required their own instrumentation. The introduction of the qPlus force sensor, a self-sensing quartz cantilever with a stiffness of about 2 kN/m [1] enabled combined STM and AFM capability, allowing highly precise imaging and spectroscopy functions and measuring the forces that act during atomic manipulation [2]. While STM had better spatial resolution than AFM in the past, the situation is reversed now with modern AFM [3]. The AFM image below, recorded at low temperature in vacuum, shows one Fe trimer next to a dimer on Cu (111) [4]. The qPlus technique used here also allows true atomic resolution in ambient conditions where the tip penetrates a liquid adsorption layer [5] and initial tests to probe through thick liquid layers were successful. Therefore, combined STM and AFM using the qPlus sensor in electrochemical environments is a promising venture.

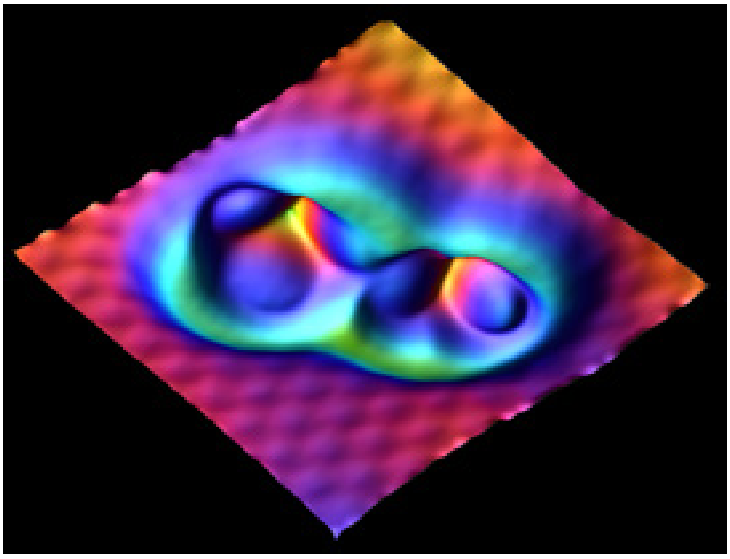

Figure 1. AFM image of a Fe trimer next to a Fe dimer on Cu(111) [4].

References

[1] F. J. Giessibl, Appl. Phys. Lett. 73, 3956 (1998).
[2] M. Ternes et al., Science 319, 1066 (2008).
[3] J. Welker, F. J. Giessibl, Science 336, 444 (2012).
[4] M. Emmrich et al., Science 348 308 (2015).
[5] D. Wastl, J. Weymouth, F. J. Giessibl, Phys. Rev. B 87, 245415 (2013).

T08

Transmission surface diffraction: a novel method for operando studies of electrochemical interfaces

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A new surface diffraction method for in situ studies of electro¬chemical interfaces is presented, which employs synchrotron X-ray radiation of high photon energy and a transmission geometry where the X-ray beam passes through the sample. Transmission surface diffraction (TSD) is a powerful and user-friendly method that enables simultaneous imaging of the full in-plane structure of solid surfaces. It further-more allows surface X-ray diffraction studies with micro¬meter spatial resolution, opening up the way to map the atomic interface structure of spatially inhomogeneous systems or to study the surface properties of small samples. The feasibility of this approach is demonstrated by TSD measurements of Co electro¬deposition on Au(111) electrodes, performed at beamline ID 31 of the ESRF. The formation of the Co crystal truncation rods (CTRs), shifts in the Au CTRs due to epitaxial strain, and the disappearance of the rods corresponding to the (22 × √3) phase of the Au surface reconstruction can be directly observed without lengthy searches in reciprocal space. In addition, in situ microscale mapping of the deposit and substrate properties and studies during Co dissolution are discussed.

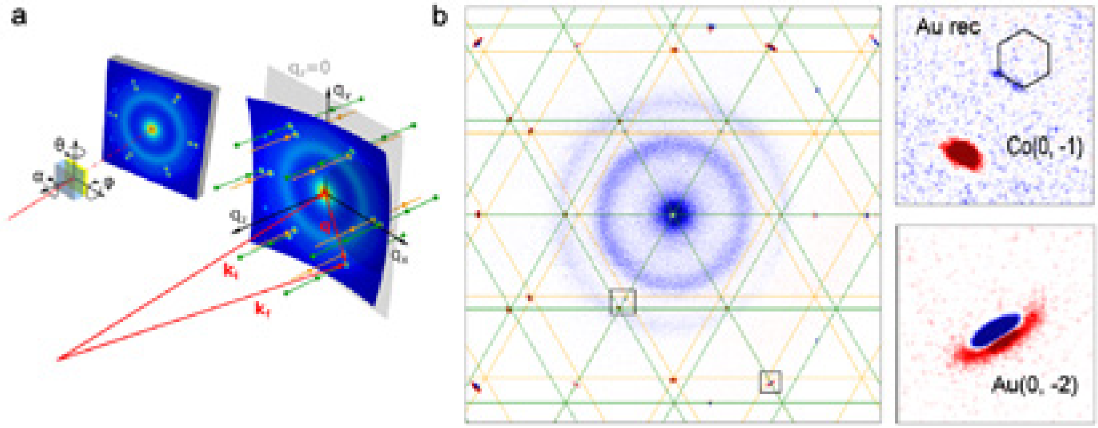

Figure. 1 (a) Real space and reciprocal space geometry of TSD. (b) In situ TSD of Au(111) in 0.1 M $NaClO_4$ + 1.3 mM HCl + 1mM $CoCl_2$, recorded at 40 keV. Shown is the intensity difference between detector images of the Au sample at -0.2 VAg/AgCl and after electrodeposition of a 20 ML thick epitaxial Co(001) film at -1.05 VAg/AgCl.

T09

Ohmic microscopy: Further Developments and Future Prospects

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Analyses of spatially-resolved ohmic microscopy measurements [1],[2],[3],[4] involving a polycrystalline Pt disk electrode embedded in an insulating surface were found to yield quantitative agreement between theory and experiment. Our efforts are currently being focused toward assessing the spatial resolution of this technique by employing facetted Pt single crystals grown by melting/cooling techniques The ohmic response, which represents a direct measure of the current flowing through a small area of the electrode, has confirmed the presence of individual facets on the Pt single crystal bead with clear Pt (111) and (100) orientation.

Shown in Figure 1 (upper panel) is the cyclic voltammogram of the facetted Pt single crystal in 0.1M H_2SO_4 recorded at a scan rate v = 10 V/s displaying a hydrogen adsorption|desorption region characteristic of polycrystalline Pt in this electrolyte. Close inspection of the voltammogram at more positive potentials revealed the presence of two small peaks centered at about 0.45 V vs RHE which are unique to the (111) surface. Significant differences were observed in the $\Delta\varphi_{sol}$ vs E curves recorded simultaneously (see black curve in the lower panel, **Fig. 1**) where the features associated with the (111) face can be clearly discerned based on a comparison with the voltammogram of a genuine Pt(111) electrode (see red curve in lower panel, **Fig. 1**).

This work was supported by a Grant from NSF CHE-1412060.

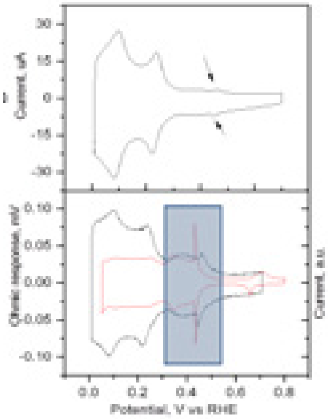

Figure 1. Cyclic voltammetry (Upper Panel) obtained at 10 V/s in 0.1M H_2SO_4 solution, $\Delta\varphi_{sol}$ vs E (black curve lower Panel) recorded simultaneously with the microreference electrodes facing at a close distance the center of the Pt(111) microfacet, and Cyclic voltammetry of genuine Pt(111) electrode collected in 0.5M H_2SO_4 solution at 50mV/s (Red Curve, lower Panel).[5]

References

[1] Cartier CA, Kumsa D, Feng Z, Zhu H, Scherson DA, Anal.Chem. 84 (2012), 7080
[2] Chen Y , Belianinov A, Scherson D.A, J. phy. Chem. C, 112 (2008), 8754
[3] Ignatowitz M, Oesterschulze E, Applied physics letters, 101 (2012), 251601
[4] Plettenberg I, Wittstock G, Electrochim. Acta,(2015), http://dx.doi.org/10.1016/j.electacta.2015.12.033
[5] Feliu JM, Orts JM, Gómez R, Aldaz A, Clavilier J. J. Electroanal. Chem 372(1994),265

T10

Dealloying in 2D: Role of the local atomic environment

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Dealloying corresponds to the dissolution of the less noble element of the alloy [1]. The phenomenon is now well understood and is extremely useful to realize metal sponges [2,3]. In this work we investigate by in–situ scanning tunneling microscopy (STM) potential controlled dealloying of 2D bimetallic alloy monolayers (Fig. 1). The presentation will focus on dealloying of Ni_xPd_{1-x} [4] monolayers prepared by co-electrodeposition on Au(111) which microstructure is close to a solid solution for all compositions. It will be shown that dealloying in 2D is somewhat different from its counterpart in 3D. A new passivation phenomenon is observed that depends on the ML composition. Dealloying onset potential is independent of Pd content below 40% but strongly varies with the number of Pd nearest neighbors for a Pd content > 40%, a behavior again different with respect to dealloying in 3D.

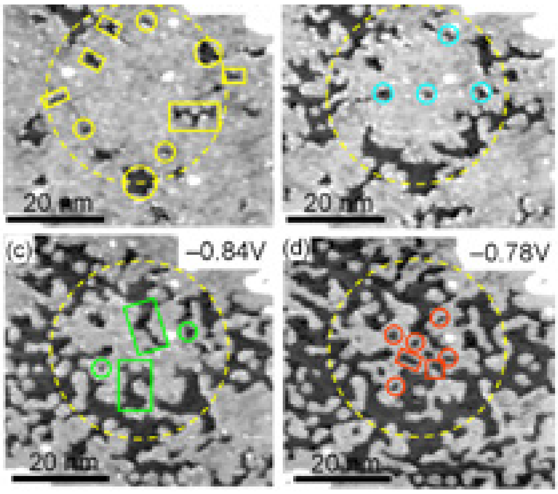

Figure 1. In situ STM images showing dealloying of a $Ni_{50}Pd_{50}$ alloy ML after successive potential steps. At each potential, the newly formed holes are indicated by circles or rectangles.

References

[1] Jonah Erlebacher, Michael J. Aziz, Alain Karma, Nikolay Dimitrov, and Karl Sieradzki, Evolution of nanoporosity in dealloying, Nature 410, 450 (2001).

[2] Yi Ding and Jonah Erlebacher, Nanoporous Metals with Controlled Multimodal Pore Size Distribution, Journal of the American Chemical Society 125, 7772 (2003).

[3] Zhonghua Zhang, Yan Wang, Zhen Qi, Wenhua Zhang, Jingyu Qin, and Jan Frenzel, Generalized Fabrication of Nanoporous Metals (Au, Pd, Pt, Ag, and Cu) through Chemical Dealloying, The Journal of Physical Chemistry C 113, 12629 (2009).

[4] A. Damian, I. Braems, F. Maroun, and P. Allongue, Electrodeposition of NiPd monolayer on Au(111): An in situ scanning tunneling microscopy study, Electrochim. Acta 112, 824 (2013).

T11

A clockwork lotus: electrochemical switching of boron nitride nanomesh wetting

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On Rh(111), a monolayer of hexagonal boron nitride (*h*-BN) forms a so-called nanomesh superstructure [1], Figure 1, characterised by a 3.2-nm lattice constant and strong electronic corrugation, which can be used for trapping atoms and molecules [2,3].

Here, we show that hydrogen underpotential deposition (H upd) is easier on *h*- BN/Rh(111) than on the naked substrate [4], and leads to submonolayer quantities of hydrogen intercalated between the *h*-BN overlayer and Rh(111), as demonstrated by electrolyte-to-vacuum transfer experiments and thermal desorption spectroscopy. In situ STM measurements reveal that the intercalation lifts the corrugation of the nanomesh, and that this process is fully reversible under potential control.

By measuring dynamic contact angles of an electrolyte drop, we show that the microscopic change within the 2-dimensional material leads to a macroscopic effect related to a 10% change in adsorption energy [4]. The static friction on the other hand, which can be extracted by extending the Young equation for non-equilibrium effects, remains unchanged for the surface in the two states.

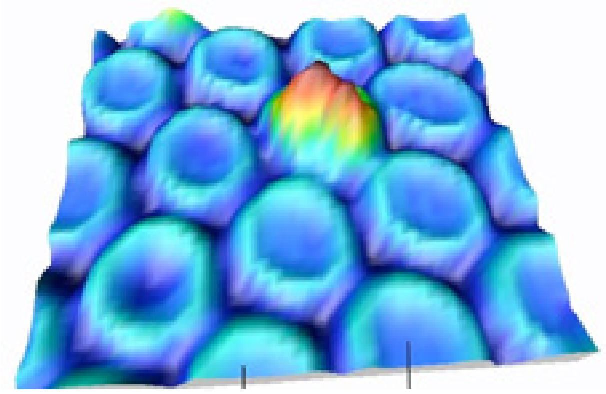

Figure 1. Three-dimensional view of the boron nitride nanomesh with one Cu- phthalocyanine molecule trapped in a pore.

References

[1] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, et al. Science 303 (2004) 217–220.
[2] S. Berner, M. Corso, R. Widmer, et al. Angew. Chem., Int. Ed. 46 (2007) 5115–5119.
[3] H. Dil, J. Lobo-Checa, R. Laskowski, P. Blaha, et al. Science 319 (2008) 1824–1826.
[4] S. F. L. Mertens, A. Hemmi, S. Muff, O. Gröning, S. De Feyter, J. Osterwalder, T. Greber Nature (2016) in press.

3 Fundamentals of Electrocatalysis

T12	Redox electrocatalysis on "floating" metallic particles	*Hubert H. Girault*
T13	Proton-coupled electron transfer in electrocatalysis	*Marc T. M. Koper*
T14	Characterising the Pt-electrolyte interface in PEM fuel cells	*Anusorn Kongkanand*
T15	Strucutre and reactivity of hybrid materials for electrocatalytic, bioelectrocatalytic and photoelectrochemical reduction of carbon dioxide	*Pawel J. Kulesza*
T16	Understanding the strucutre sensitivity of electrocatalytic reactions in simple terms	*Frederico Calle-Vallejo*
T17	Electrochemical reduction of CO_2-catalyzed by cobalt porphyrin complexes: a mechanistic study from DFT	*Adrien Göttle*
T18	A scenario for oxygen reduction in alkaline media	*Wolfgang Schmickler*

Chairs: Prof. Elena R. Savinova and Prof. Kohei Uosaki

T12

Redox electrocatalysis on “floating” metallic particles

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Redox electrocatalysis on floating metallic particles can be defined as the catalytic role played by a metallic particle in a solution containing two redox couples. The role of the particle is to act as an electron relay between the donor and the acceptor.

We shall fist discuss how the Fermi level of the metallic particles adapts to the local redox environment and discuss how the classical electrochemical methodology can be applied to study these reactions.

We shall then illustrate with two examples. First, redox electrocatalysis using gold nanoparticles adsorbed at a liquid-liquid interface promoting the electron transfer reactions between an aqueous and a non-aqueous redox couple.

The second example is the oxidation of Vanadium(II) in sulfuric acid solutions on Mo_2C particles [1]. This reaction is of industrial interest as it can be used to produce hydrogen on demand and at high pressures using a Vanadium redox flow battery. Here, the mono-electron transfer oxidation on Vanadium(II) is fast compared to the reduction of the proton and the Fermi level of the electron in the catalyst is fixed by the Nernst equation for the V(II)/V(III) couple.

We shall present results form a pilot-plant operating on this principle using a 10kW/40kWh Vanadium redox flow battery and producing a kilo of hydrogen a day.

References

[1] All-vanadium dual circuit redox flow battery for renewable hydrogen generation and desulfurization, P. Peljo, H. Vrubel, V. Amstutz, J. Pandard, J. Morgado, A. Santasalo-Aarnio, D. Lloyd, F. Gumy, C.R. Dennisson, K. Toghill and H.H. H. Girault, Green Chemistry, DOI: 10.1039/c5gc02196k

T13

Proton-coupled electron transfer in electrocatalysis

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Many electrocatalytic reaction of contemporary interest involve the transfer of multiple protons and electrons. Understanding the factors controlling the concertedness of proton-electron transfer in the elementary steps of the reaction mechanisms is very important in finding the right conditions of the electrode-electrolyte interface for optimal catalysis. Both the nature of the catalysts ànd the electrolyte have an important role in defining the highest overall reaction rate. I will outline some of the main aspects of the theory of proton-coupled electron transfer and illustrate its implications and manifestations for a variety of important electrocatalytic reactions, such as CO2 reduction, oxygen reduction, ammonia oxidation, formic acid oxidation, etc.

T14 Characterizing the Pt-Electrolyte Interface in PEM Fuel Cells

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Great progress in reducing platinum loadings in a proton-exchange-membrane fuel cell cathode. However, a large performance loss is often observed at high-current density on low-Pt-loaded electrodes. This large loss is apparently caused by the presence of a resistance at or near the catalyst-ionomer interface [1]. Implementation of ionomers designed to interact with Pt in a way that does not constrain oxygen reduction reaction rates is thus an important research goal. However, improved tools to quantify and characterize this interaction are first needed to enhance our understanding of this resistance and correlate it with performance loss.

Here we take a note of the CO displacement method that Feliu et al. [2] developed in the early 1990's on Pt single crystals for measuring adsorbed ion charges in aqueous electrolyte. We have validated the principle on polycrystalline Pt and carbon-supported Pt nanoparticles, and we now are able to implement the principle in a fuel cell. Figure 1 shows current transient during chronoamperometry as CO gas is being introduced to the electrode (t = 120 s). At ≤0.2 V, the adsorbates on Pt are primarily protons, hence a positive current is measured. At >0.3V, a negative current is measured indicating adsorption of a negatively charged species - likely the sulfonate group of the ionomer. One can then quantify the adsorption amount by integrating the charge at each potential (inset). In this manner, ionomer adsorption for various ionomer types at different operating conditions can be examined. Correlation of the measured charges with fuel cell performance as well as the effect of ageing on the Pt-ionomer interface will be discussed.

This work was partially supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under grant DE-EE0007271.

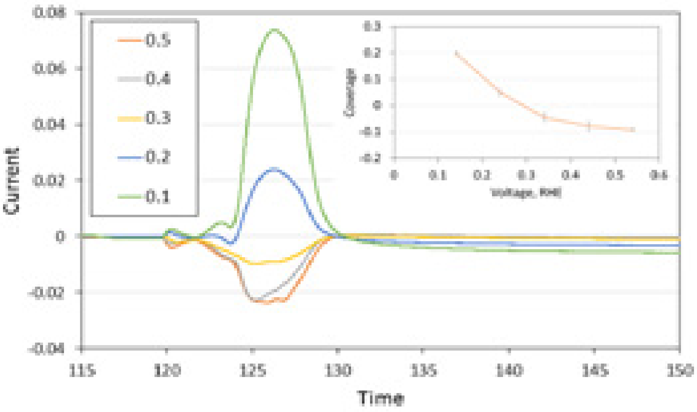

Figure 1. Chronoamperometry at different voltages after CO gas is introduced.

References

[1] Kongkanand A, Mathias MF. J. Phys. Chem. Lett. (2016) in press.
[2] Feliu JM, Orts JM, Gomez R, Aldaz A, Clavilier J. J. Electroanal. Chem. 372 (1994) 265.

T15

Structure and reactivity of hybrid materials for electrocatalytic, bioelectrocatalytic and photoelectrochemical reduction of carbon dioxide

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There has been growing interest in the electrochemical reduction of carbon dioxide, a potent greenhouse gas and a contributor to global climate change. Given the fact that the CO_2 molecule is very stable, its electroreduction processes are characterized by large overpotentials. To produce highly efficient and selective electrocatalysts, the transition-metal-based molecular materials are often considered. It is believed that, during electroreduction, the rate limiting step is the protonation of the adsorbed CO product to form the CHO adsorbate.

To optimize the hydrogenation-type electrocatalytic approach, we have proposed to utilize nanostructured metallic palladium in a form of highly dispersed and reactive nanoparticles generated within supramolecular network of N-coordination complexes [1]. Reduction of carbon dioxide begins now at less negative potentials and is accompanied by significant enhancement of the CO_2-reduction current densities. Among important issues are specific interactions between nitrogen coordinating centers and metallic palladium sites.

We have also explored the ability of biofilms to form hydro-gel-type aggregates of microorganisms attached to various surfaces including those of carbon electrode materials. Biofilms are able to transfer electrons to and from electrodes, and they can act in a manner analogous to redox or conducting polymer films on electrodes. Here we have explored a biofilm formed by a strain of Yersinia enterocolitica as active bioelectrocatalytic support [2]; it is characterized by long-term stability over wide ranges of pH (4-10) and temperatures (0-40°C). Upon incorporation of various noble metal nanostructures and/or conducting polymer ultra-thin films, a highly reactive and selective system toward CO2-reduction is obtained.

Another possibility to enhance electroreduction of carbon dioxide is to explore direct transformation of solar energy to chemical energy using transition metal oxide semiconductor materials. We show here that, by intentional and controlled combination of metal oxide semiconductors, we have been able to drive effectively photoelectrochemical reduction of carbon dioxide. The combination of titanium (IV) oxide (TiO2) and copper (I) oxide (Cu_2O) has been explored toward the reduction of CO_2 before and after illumination. Application of the hybrid system composed of both oxides has resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol, as demonstrated upon identification of final products using conventional and mass-spectrometry-assisted gas chromatography. A role of TiO2 is not only stabilizing: the oxide is also expected to prevent the recombination of charge carriers.

References

[1] Wadas A, Rutkowska IA,…. Kulesza PJ. Electrocatalysis 5 (2014) 229-234.
[2] Seta E, Lotowska W, Rutkowska IA, Wadas A,…. Kulesza PJ. Aust. J. Chem. (2016) – in press (DOI: 10.1071/CH15744).

T16

Understanding the structure sensitivity of electrocatalytic reactions in simple terms

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Numerous heterogeneous electrocatalytic reactions are structure sensitive [1]. This means that among the myriad of different surface sites they possess, only certain types are catalytically active. Identifying those sites and understanding the origin of their high activities is paramount for the design of enhanced electrocatalysts. In this talk, I will briefly analyze the different structure sensitivities of the oxygen reduction reaction to water on Pt and Au [2], CO and acetaldehyde reduction to C_2 products on Cu [3, 4], dimethyl ether oxidation on Pt [4, 5] and hydrogen evolution on Pt [6].

I will show that for all those different reactions and catalysts, it is possible to use simple coordination considerations to understand activity trends among different surface facets and extract simple conclusions to design highly active sites in electrocatalysis. Based on the correlation between surface energetics and coordination, I will explain why the oxygen reduction prefers (111) terraces on Pt and
(100) terraces on Au, why CO reduction and dimethyl ether oxidation prefer square ensembles of sites while steps are most active for acetaldehyde reduction, and why polycrystalline Pt is more active than Pt(111) for hydrogen evolution. Finally, I will show that the exceptions to the general correlation between surface energetics and coordination result in highly active sites that break scaling relations between chemisorption energies (Fig. 1) [4, 7].

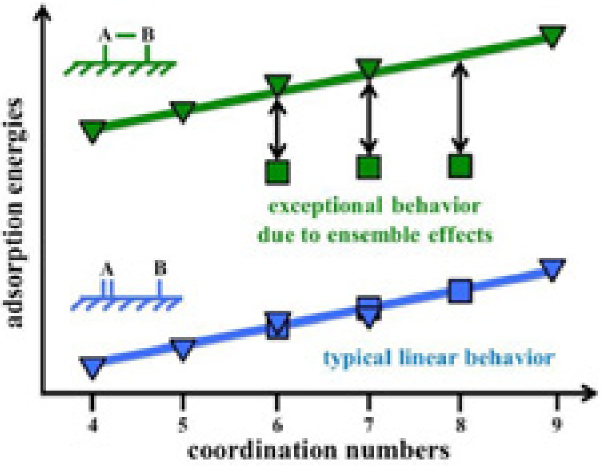

Figure 1. Adsorption-energy trends described by coordination numbers. The exceptions are highly active sites that break scaling relations. Adapted from [4].

References

[1] Koper MTM. Nanoscale 3 (2011) 2054-2073.
[2] Calle-Vallejo F et al. Science 350 (2015) 185-189.
[3] Calle-Vallejo F, Koper MTM. Angew Chem. 125 (2013) 7423-7426.
[4] Li HJ, Li Y, Koper MTM, Calle-Vallejo F. J. Am. Chem. Soc. 136 (2014) 15694-15701.
[5] Li et al. J. Am. Chem. Soc. 135 (2013) 14329-14338.
[6] Tymoczko J, Calle-Vallejo F, Schuhmann W, Bandarenka AS. Nat Comms (2016).
[7] Calle-Vallejo F, Loffreda D, Koper MTM, Sautet P. Nat. Chem. 7 (2015) 403–410.

T17

Electrochemical reduction of CO2 catalyzed by cobalt porphyrin complexes: a mechanistic study from DFT.

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The electrochemical reduction of CO_2 is a promising way to use the electric energy gathered from sustainable resources for the production of valuable chemicals. [1] We have recently shown that a cobalt porphyrin catalyst immobilized on an inert electrode is able to efficiently reduce CO_2 to CO (pH=3) in water and, can also produce small amount of methane at low pH (pH=1). [2] In order to better understand mechanistic details that govern the output of this reaction, we have performed a theoretical investigation, using DFT calculations, to unravel the various pathways that lead to the reduction products. [3] Especially, we have highlighted that at the onset potential of the CO2 reduction, all the electrochemical steps that lead up to the formation of methane are thermodynamically favourable (Fig. 1). This is consistent with experimental observations and points out the crucial role of the pH in the selectivity.

Furthermore, we have also addressed the reliability of a simple method based on an isodesmic proton exchange reaction to compute accurate pKa of metal-bonded reaction intermediates, and show how it can be used within the framework of a theory recently proposed to predict the sequential or concerted nature of proton-coupled electron transfer reactions. [4]

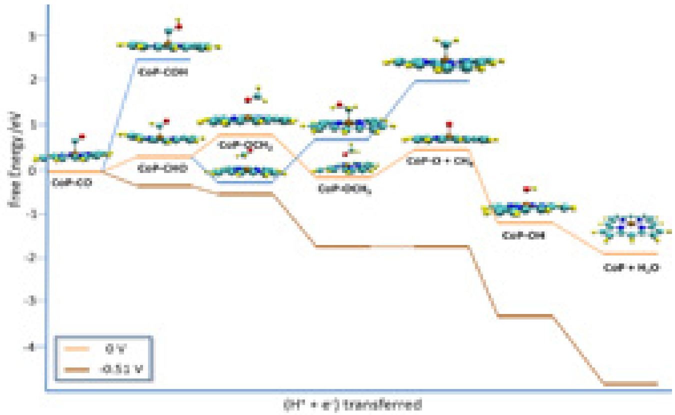

Figure 1. Possible pathways for CH_4 formation from the CO adduct. Most favourable pathway at applied potential U=0 V_{RHE} (orange line) and U=-0.51 V_{RHE} (brown line).

References

[1] Aresta M, Dibenedetto A, Angelini A. Chem. Rev.114 (2014) 1709-1742.

[2] Jing S, Kortlever R, Kas R, Birdja YY, Diaz-Morales O, Kwon Y, Ledezma-Yanez I, Schouten KJP, Mul G, Koper MTM. Nat. Comm. 8 (2015) 8177

[3] Jing S, Manuel K, Göttle A, Koper MTM. J. Phys. Chem. C. (2016) article ASAP DOI: 10.1021/acs.jpcc.5b10763

[4] Koper MTM. Phys. Chem. Chem. Phys. 15 (2013) 1399

T18

A scenario for oxygen reduction in alkaline media

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We investigate oxygen reduction in alkaline solutions with the focus on gold and silver electrodes. On the basis of theoretical considerations we propose the following mechanism, which we support by explicit calculations on the basis of our own theory:

$$O2 + e^- \rightarrow O_2^- \qquad (1)$$

We have performed calculations for Au(100) and Ag(100) and conclude that this is a slow reaction that occurs in an outer sphere mode.

$$O2^- + H_2O + e^- <-> HO_2^- + OH^- \qquad (2)$$

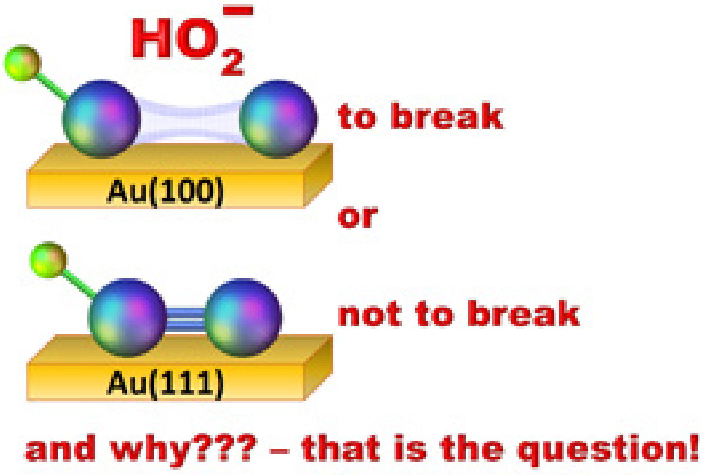
A fast reaction in an outer sphere mode with a very small energy of activation.

$$HO_2^- + H_2O \rightleftharpoons 2OH_{(ad)} + OH^- \qquad (3)$$

A chemical reaction whose free energy depends strongly on the adsorption energy of OH. Expected to be fast on Au(100).

$$OH_{ad} \rightarrow OH^- \qquad (4)$$

A fast reaction; the adsorption energy is much more favorable on Au(100) than on Au(111). We suggest that for this reason reaction (3) takes place on Au(100), but not on Au(111); so on the latter surface the oxygen-oxygen bond is not broken at small overpotentials. This explains, why Au(100) is such a good catalyst.



Reference:

A. Ignaczak, R.R. Nazmutdinov, A. Goduljan, L.M. de Camüos Pinto, F. Juarez, P. Quaino, E. Santos, and W. Schmickler, Nano Energy, DOI: nanoen.2016.06.001

4

Applied Electrochemistry

T19	Electrochemistry of viologens: New perspectives	*Takamasa Sagara*
T20	Electrochemical detection of gallic acid in mild neutral solutions using conducting polymer film-modified electrodes	*Shu-Hua Cheng*
T21	Electrochemical crosslinking of hydrongen adhesives	*Richard O'Rorke*
T22	Pt-Ni-SU-8 microrocket with steerable trajectory using eccentric Pt nanoengine	*Liangxing Hu*

Chair: Prof. Petr Krtil

T19

Electrochemistry of Viologens: New Perspectives

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Viologens, a family of compounds of diquaternized 4,4'-bipyridine, are the major electron transfer mediators to be listed right along with ferrocenyl compounds. Unless being exposed alkaline while hot, viologens are quite stable. They are featured by reversible redox reaction, three oxidation states including dication (V^{2+}), radical cation ($V^{+\bullet}$), and di-reduced forms, and marked color change to blue when producing $V^{+\bullet}$. Based on the oxidation state dependent sharp change in affinity with host compounds, viologen appears also as a dynamic unit in supramolecules.

In addition, dimerization of $V^{+\bullet}$ as well as oxidation state dependent solubility and interaction with anions provide us with rich and new opportunities to use viologens as dynamically controllable units in electrochemistry.

Here, we report on active uses of viologens in;

(1) Electroactive self-assembled monolayer (SAM) of viologen-thiol on an Au electrode: The low dielectric environment in the SAM facilitates electrostatic binding between V^{2+} and soft anions, further effecting the chain-chain interaction with anionic surfactants.

(2) Two dimensional redox phase transition control: Intermolecular interaction by dimerization of $V^{+\bullet}$, chain-chain paralleling, and hydrogen-bonding formation between functional groups, together with dehydration upon the reduction of V^{2+} to $V^{+\bullet}$ result in the first-order phase transition on HOPG and Au(111) electrodes, and the adlayer structures are determined by interplay with anions.

(3) Inclusion of viologens in hydrogels: Covalent attachment of viologen to a hydrophilic polymer produced highly $V^{+\bullet}$-dimer rich state upon reduction.

(4) Synthesis and characterization of viologen ionic liquids: Salt of bis(fluoro-alkylsulfonyl) imide type anions with viologens bearing well-designed side chains appeared as a new class of redox active ionic liquid [5], and some of them are characterized crystallographically [6] and spectroelectrochemically.

Viologens still find new applications at electrified interfaces, especially as a dynamically controllable unit. Experimental results will be used to discuss the new perspectives of these applications.

References

[1] Higashi T, Shigemitsu Y, Sagara T, Langmuir 27 (2011) 13910-13917.
[2] Higashi T, Sagara T, Langmuir 29 (2013) 11516-11524.
[3] Higashi T, Sagara T, Electrochim. Acta 114 (2013) 105-115.
[4] Higashi T, Kawamoto T, Yoshimoto S, Sagara T, J. Phys. Chem. C, 119 (2015) 1320-1329.
[5] Bodappa N, Broekmann P, Fu Y, Furrer J, Furue Y, Sagara T, Siegenthaler H, Tahara H, Vesztergom S, Zick K, Wandlowski Th, J. Phys. Chem. C, 119 (2015) 1067-1077.
[6] Tahara H, Furue Y, Suenaga C, Sagara T, Cryst. Growth Des. 15 (2015) 4735-4740.

T20

Electrochemical detection of gallic acid in mild neutral solutions using conducting polymer film-modified electrodes

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Gallic acid (3,4,5-trihydroxybenzoic acid, GA) is comprehensively present in green tea, black tea, grapes and plants [1]. Due to its powerful antioxidant and antiradical activity, GA has received considerable attention for reserachers. GA solution is generally accepted as a reference standard to determine the total polyphenolic content in plants, and the resultant GA equivalents are used to indicate the antioxidant level of the plant extracts [2]. In the previous reports, the direct electrochemical oxidation of GA can be observed at bare electrode substrates such as GCE, ITO and Pt, and the electrodes modified with various types of inorganic and organic nanocomposites. Generally, acidic solutions (pH 2-3) are used as the optimal electrolytes for analysis of GA using an electrochemical oxidation approach [3-4].

In this work, two types of electrochemical sensors are developed, targeting the determination of gallic acid (GA) in a mild neutral condition, in contrast to the existing electrochemical methods. The pre-anodized screen-printed carbon electrodes were used as the electrode substrates (SPCE*), which were modified with either poly(melamine) film (PME, the first sensor) or poly(caffeic acid) film (PCA, the second sensor). The surface characteristics of the sensing surface were well-characterized by field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS) and surface water contact angle experiments. The electrochemical activity of the sensing surface was investigated by cyclic voltammetry and electrochemical impedance techniques. The results indicated that GA could be detected in aqueous solutions over a wide pH range at the two electrochemical sensors. Several experimental parameters were optimized, and the proposed assay exhibits a wide linear response to GA not only in acidic solutions but also in neutral solutions. The electrochemical system also showed high stability for replicate determination of GA. The interference effects from some inorganic salts and orthodiphenolic compounds were also investigated. The proposed method was applied to detect GA in green tea samples using the standard addition method, and the results were compared with a conventional Folin-Ciocalteu method.

References

[1] Thompson, MA, Collins, PB, Handbook on Gallic Acid: Natural occurrences, antioxidant properties and health implications 2013 (Nova Science Pub Inc, New York).

[2] Blainski A, Lopes, G, Mello J,Molecules 18 (2013) 6852-6865.

[3] Kahl M, Golden TD, Electroanalysis 26 (2014) 1664-1670.

[4] Abdel-Hamid R, Newair EF, J. Electroanal. Chem. 704 (2013) 32-37.

T21

Electrochemical crosslinking of hydrogel adhesives

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Adhesives are typically cured either by heating, UV light or a rapid chemical reaction on mixing multiple components. Such curing mechanisms are difficult to control once initiated, give little scope to tune properties such as elasticity and adhesive strength, and are limited in application to specific materials.

We present an adhesive that crosslinks at low-voltage via electrochemical activation of adhesive functional groups [1]. Poly amido amine (PAMAM) dendrimers are modified with carbene precursor functional groups (aryl diazirines), which are electrochemically reduced at low voltage, triggering both inter-molecular and adhesive-surface crosslinking.

Unlike conventional electrochemical polymerization, the curing process does not passivate the electrode and crosslinking occurs throughout the material. Furthermore, crosslinking stops as soon as the voltage is removed, allowing material properties and adhesion to be tuned. Shear storage modulus up to 50 kPa and lap-shear adhesion strengths up to 8 Ncm^{-2} can be achieved with our adhesive by tuning the density of carbene precursors, the modified dendrimer concentration and the activation time.

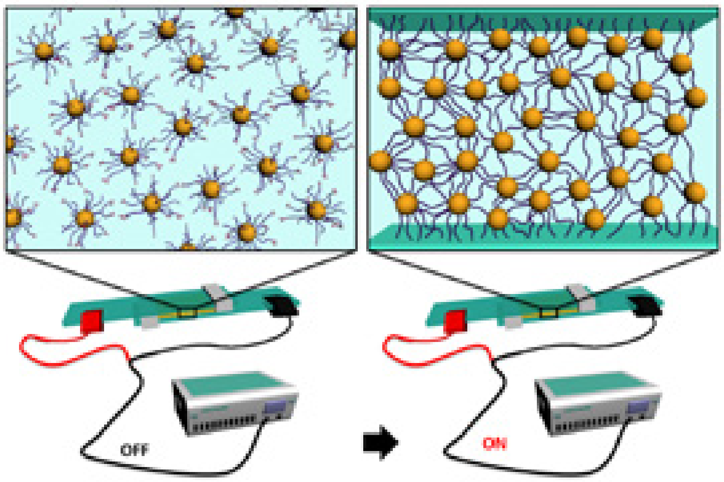

Figure 1. Electrocuring adhesive concept [1]; dendrimer molecules modified with carbene precursor adhesive functional groups undergo inter-molecular and molecule-surface crosslinking upon low-voltage stimulation.

References

[1] Ping J. et al, Nature Communications 6 (2015), 8050.

T22

Pt-Ni-SU-8 microrocket with steerable trajectory using eccentric Pt nanoengine

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Launch vehicles can control their motion direction via ejecting the combusted fuel in the space and bio-molecular motor proteins possess the ability to walk along the tracks through hydrolyzing adenosine triphosphate (ATP) molecules in various types of living organisms [1]. Inspired by man-made launch vehicles and naturally occurring bio-molecular motor proteins, self-propelling microrockets are proposed, which consist of polymer SU-8, central magnetic nickel (Ni) and catalytic platinum (Pt). It is for the first time that the polymer material is used as the composition of the microrockets. This innovative type of Pt-Ni-SU-8 catalytic microrockets are designed and fabricated using an easy-operation layer-by-layer deposition method based on nano-electro-mechanical systems (NEMS) technology, whereby the eccentric Pt nanoengine functions as the chemical catalyst for the decomposition of hydrogen peroxide (H_2O_2) to produce oxygen (O_2) bubbles detaching from the surface and water (H_2O), which in turn introduces an off-center recoil force Fdrive thrusting the microrockets propelling forward circularly [2], as shown in Figure 1. Moreover, the microrocket's motion is experimentally characterized in different concentrated H_2O_2 solution, revealing that the O_2 bubbles are initially generated from the surface of Pt and detached from the microrockets after a period of time. The results show that the motion speeds of the microrockets increase with the increment of H_2O_2 concentration. In addition, the novel microrockets can autonomously propel forward circularly in an either clockwise or a counter-clockwise direction.

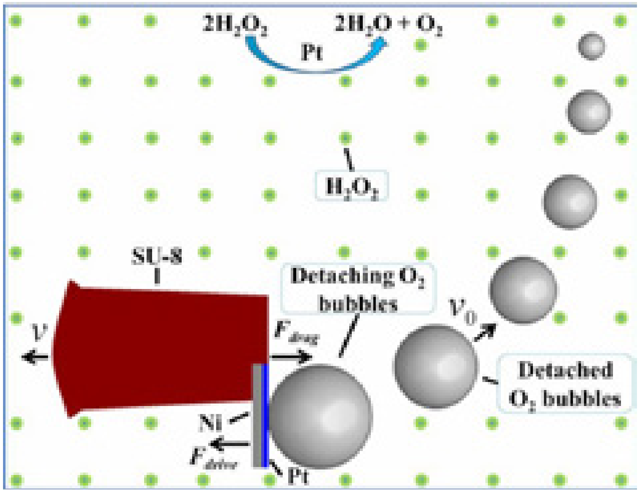

Figure 1. Demonstration of the circular propulsion mechanism of Pt-Ni-SU-8 microrocket in H2O2 solution. The microrocket propels forward circularly at a speed of v, because the detached O2 bubbles with a speed of v0 are only distributed on one side of the horizontal axis of the rocket, thus the generated recoil force Fdrive and drag force Fdrag are not aligned.

References

[1] Schmidt C, Vogel V. Lab Chip 10 (2010) 2195-2198.
[2] Hu LX, Miao JM, Grüber G. RSC Adv. 6 (2016) 3399-3405.

6

Electrocatalysis towards OER and ORR

T23

Understanding oxygen electrocatalysis on transition metal oxides

Elena R. Savinova

T24

Bifunctional ORR and OER electrocatalysis for metal-oxygen batteries: role of the catalyst

Helmut Baltruschat

T25

Oxygen electrocatalysis on transition metal spinel oxides

Zhichuan Xu

T26

Accelerating oxygen reduction on alloys of Pt and rare earths

Ifan E. L. Stephens

T27

Defects do catalysis: CO monolayer oxidation and oxygen reduction reaction on hollow PtNi/C nanoparticles

Frédéric Maillard

T28

Iridium-based double perovskites for efficient water oxidation

Oscar Diaz-Morales

T29

Effect of ad-atoms on reconstruction of shape-controlled Pt nanoparticles

Devivaraprasad Ruttala

Chairs: Prof. Wolfgang Schmickler and Prof. Jason Boon Siang Yeo

T23

Understanding Oxygen Electrocatalysis on Transition Metal Oxides

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Transition metal oxides (TMOs) play an important role in state-of-the-art technologies. One of the emerging applications of TMOs is related to the conversion and storage of renewable energies. In this context TMOs are attracting an increasing attention as promising materials for oxygen electrode in polymer electrolyte fuel cells, electrolyzers, and metal-air batteries.

This presentation will be mostly devoted to the Mn and Co-oxide catalyzed oxygen reduction reaction (ORR). We will first show that the measured ORR activity strongly depends on the addition of carbon which is introduced in the catalytic layers for improving their electronic conductivity [1], and that not only the amount of carbon binder, but also its type is essential. We will then discuss the mechanism of the ORR. We complement an experimental rotating ring disc electrode investigation of the ORR with the rotating disc electrode study of the oxidation/reduction of the stable ORR intermediate, hydrogen peroxide, and combine these with microkinetic modeling in order to arrive at a self-consistent model of the ORR on TMOs oxides [2-4]. We will further demonstrate that for Mn oxides the potential of the Mn(III/IV) red-ox transition of surface cations can be used as a descriptor of their catalytic activity in the ORR [4]. We will then show that the reaction mechanism and the selectivity for the 4e- ORR depend on the structure and the composition of Mn oxides. Finally, we propose a tentative explanation for the discovered relationship between the catalytic activity and the crystalline structure and propose means to tune the electrocatalytic activity.

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References

[1] T. Poux, F. Napolskiy, G. Kéranguéven, S. Istomin, G. Tsirlina, E. Antipov, E. R. Savinova, Catal. Today, 189 (2012) 83–92.

[2] T. Poux, A. Bonnefont, A. Ryabova, G. Kéranguéven, G.A. Tsirlina, E.R. Savinova, Phys. Chem. Chem. Phys., 16 (2014) 13595-13600.

[3] T. Poux, A. Bonnefont, G. Kéranguéven, G.A. Tsirlina, E.R. Savinova, ChemPhysChem, 15(2014) 2108-2120.

[4] A. S. Ryabova, F. S. Napolskiy, T. Poux, S. Y. Istomin, A. Bonnefont, D. Antipin, A.Y. Baranchikov, E. Levin, A. M. Abukamov, G. Kéranguéven, E. V. Antipov, G. A. Tsirlina, E. R. Savinova, Electrochimica Acta, 187 (2016) 161-172.

T24

Bifunctional ORR and OER Electrocatalysis for Metal-oxygen Batteries: Role of the Catalyst

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For metal air batteries, a highly reversible electrocatalyst is needed, i. e. a catalyst for both OER and ORR. In alkaline solution, Ag is known to be the best electrocatalyst for oxygen reduction. However, Ag is not catalyzing oxygen evolution. Spinels such as Co_3O_4 and various perovskites have been shown to be good catalysts for oxygen evolution but are not very good for oxygen reduction. We have recently shown that a particular mixture of a Ag catalyst with Co_3O_4.nanoparticles leads to a catalyst which not only combines the good performance of Ag for the ORR with that of Co_3O_4 for the OER, but shows a better activity than its components. [1,2]

Here, we will present further insights and demonstrate that this effect is also observed for various perovskites. The effect is also observed when Co_3O_4 or the perovskites are deposited on smooth Ag electrodes. Using differential electrochemical mass spectrometry (DEMS) and ^{18}O-isotope exchange has been shown in the past that during oxygen evolution at oxides the oxygen of the lattice is participating in the oxygen evolution reaction.[3-4]

In aprotic solvents, oxygen reduction leads to superoxide or peroxide, depending on the cation present. Since no bond breaking is occurring here, a dependence of the reaction on the electrocatalyst material is not expected.

We have carried out a detailed study involving DEMS, electrochemical quartz crystal micro-balance (EQCM) and the rotating disc electrode (RRDE) using a variety of smooth model electrodes (glassy carbon, different noble metals and Au(111) and found marked differences. E.g., during oxygen reduction in a Li^+ containing DMSO, reduction to superoxide and peroxide occur in well separated potential regions, whereas on Rh reduction occurs in a 2 electron process (as demonstrated by DEMS) in the whole reduction region. In the presence of Li, only a part of the formed reduction product (Li_2O_2) is deposited on the electrode, another part is dissolved in the electrolyte. From the deposit, oxygen can be evolved, the amount of which also depends on the electrode material. Whereas on Pt and Rh the oxidation occurs in only one oxidation peak (which is paralleled by oxygen evolution) close to the equilibrium potential, on Au three peaks are observed in a wide potential range. Comparative experiments using other electrolyte systems and in Mg^{2+} and other cation-containing electrolytes will also be presented.

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References

[1] H.M.A. Amin, H.Baltruschat, D.Wittmaier, K.A.Friedrich, Electrochim. Acta,151 (2015) 332.
[2] D. Wittmaier, N. Wagner, K.A. Friedrich, H.M.A. Amin and H. Baltruschat, J. Power Sources, 265 (2014) 299.
[3] M. Wohlfahrt-Mehrens and J. Heitbaum, J. Electroanal. Chem., 237 (1987) 251.
[4] S. Fierro, T. Nagel, H. Baltruschat, C. Comninellis, Electrochem. Com., 9 (2007) 1969.
[5] C. J. Bondue, A. A. Abd-El-Latif, H. P. and H. Baltruschat, J. Electrochem.l Soc. 162 (2015), A479-A487
[6] C. J. Bondue, P. Reinsberg, A. A. Abd-El-Latif, H. Baltruschat, PCCP 17 (2015), 25593

T25 Oxygen Electrocatalysis on Transition Metal Spinel Oxides

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Exploring efficient and low cost oxygen electrocatalysts for ORR and OER is critical for developing renewable energy technologies like fuel cells, metal-air batteries, and water electrolyzers. This presentation will presents a systematic study on oxygen electrocatalysis (ORR and OER) of transition metal spinel oxides.[1] Starting with a model system of Mn-Co spinel, the presentation will introduce the correlation of oxygen catalytic activities of these oxides and their intrinsic chemical properties. The catalytic activity was measured by rotating disk technique and the intrinsic chemical properties were probed by synchrotron X-ray absorption techniques. It was found that molecular orbital theory is able to well-explain their activities.[2,3] The attention was further extended from cubic Mn-Co spinels to tetragonal Mn-Co spinels and it was found that the molecular theory is again dominant in determining the catalytic activies. This mechanistic principle is further applied to explain the ORR/OER activities of other spinels containing other transition metals (Fe, Ni, Zn, Li, and etc.).

References

[1] Wei C, Feng Z, Barber J, Shao-Horn Y, Xu Z. in preparation.

[2] Suntivich J, Gasteiger, HA, Yabuuchi, N, Nakanishi H, Goodenough, JB, Shao-Horn, Y. Nat. Chem. 3 (2011) 546.

[3] Suntivich J, May KJ, Gasteiger HA, Goodenough JB, Shao-Horn Y, Science 334 (2011) 1383.

T26 Accelerating oxygen reduction on alloys of Pt and rare earths

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The slow kinetics of the oxygen reduction to H_2O impose a bottleneck against the widespread uptake of low temperature fuel cells in automotive vehicles. High loadings of platinum are required to catalyse the reaction; its short supply limits the extent to which fuel cell technology could be scaled up. The most widely used strategy to decrease the Pt loading is to alloy Pt with other late transition metals, in particular Ni or Co. However, these materials often degrade via dealloying. At our laboratory, we have developed a different class of catalyst for oxygen reduction: alloys of Pt with rare earths, such as Y or Gd. The strong interaction between Pt and the rare earth elements should make these compounds inherently less prone towards dealloying. These catalysts exhibit high activity, both on extended surfaces and in the nanoparticulate form.[1-3] Our efforts are now aimed towards the large scale synthesis of these catalysts, so that they can be implemented in fuel cells and tested for their long term stability.

In the current contribution I will provide an overview of the factors controlling the performance of this class of Pt alloy. It turns out that that the activity and stability are a function of the bulk Pt-Pt distance; this parameter, in turn, can be tuned by changing the composition of the lanthanide element, via the “lanthanide contraction”. [4] We have investigated these alloys in the form of single crystals, thin films and model size-selected nanoparticles. Our studies incorporate electrochemical measurements, ultra-high vacuum based surface science methods, electron microscopy, synchrotron-based X-ray spectroscopy and density functional theory calculations.

References

[1] J. Greeley, I.E.L. Stephens, A.S. Bondarenko, T.P. Johansson, H.A. Hansen, T.F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J.K. Nørskov, Nature Chemistry, 1 (2009) 552-556.

[2] I.E.L. Stephens, A.S. Bondarenko, U. Gronbjerg, J. Rossmeisl, I. Chorkendorff, Energy Environ. Sci., 5 (2012) 6744-6762.

[3] P. Hernandez-Fernandez, F. Masini, D.N. McCarthy, C.E. Strebel, D. Friebel, D. Deiana, P. Malacrida, A. Nierhoff, A. Bodin, A.M. Wise, J.H. Nielsen, T.W. Hansen, A. Nilsson, I.E.L. Stephens, I. Chorkendorff Nature Chemistry, 6 (2014) 732-738.

[4] M. Escudero Escribano, P. Malacrida, M.H. Hansen, U.G. Vej-Hansen, A. Velazquez-Palenzuela, V. Tripkovic, J. Schiøtz, J. Rossmeisl, I.E.L. Stephens, I. Chorkendorff, Science, (2016) in press.

T27

Defects do Catalysis: CO Monolayer Oxidation and Oxygen Reduction Reaction on Hollow PtNi/C Nanoparticles

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The catalytic performance of extended and nanometer-sized surfaces strongly depends on the amount and the nature of structural defects that they exhibit. However, whereas the effect of steps or adatoms may be unraveled with single crystals ("surface science approach"), implementing reproducibly and in a controlled manner structural defects on nanomaterials remains hardly feasible. The case of bimetallic nanomaterials, which are used to catalyze the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC), is of particular interest. Indeed, due to the large lattice mismatch between Pt and the alloying element, these bimetallic nanomaterials may contain point (vacancy), planar (dislocations and grain boundaries) and bulk defects (voids, pores). In this paper, we synthesized a set of catalysts with identical chemical composition and elemental distribution but different morphology, crystallite size and lattice strain via thermally annealing hollow PtNi/C nanoparticles under vacuum, N_2, H_2, or air atmosphere (Figure 1). By combining in situ transmission electron microscopy, electrochemical measurements, and Rietveld and pair-distribution function analyses of Synchrotron X-ray diffraction patterns, we showed that the structurally disordered areas located between individual crystallites are highly active for the electrochemical CO_{ads} oxidation and the ORR.

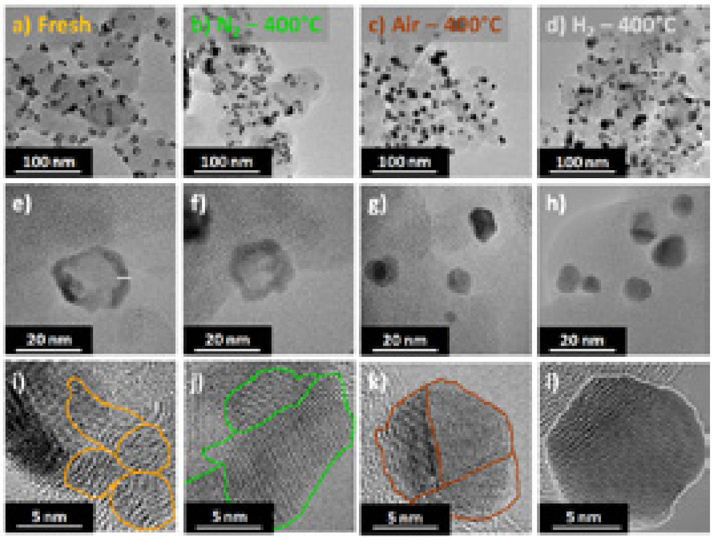

Figure 1. Conventional and aberration corrected high-resolution transmission electron microscopy images of the as-synthesized and thermally annealed PtNi/C nanoparticles. (a-d) assemblies and (e-h) HR-TEM images of the as-synthesized PtNi/C nanoparticles and after thermal annealing at 400°C under different atmospheres, respectively. Zoom-in images of the fine nanostructure of the PtNi shell are shown in (i-l). The boundaries between the individual PtNi nanocrystallites are highlighted in colour.

T28

Iridium-based Double Perovskites for Efficient Water Oxidation in Acid Media

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The development of active, cost-effective and stable anodes for the oxygen evolution reaction (OER) is one of the major challenges for the solar-to-fuel conversion towards sustainable energy generation. Iridium oxide (IrO_2) has the best compromise between OER activity and stability in acid media among all transition metal oxides [1- 2]. However, iridium is one of the rarest metals on earth, and its high price makes it unsuitable for large-scale applications. Therefore, development of active and stable OER catalysts with a lower amount of the expensive but stable iridium, in combination with iridium recycling, is an alternative avenue (and may presently well be the most realistic avenue) for multi-MW solar fuel generation using PEM electrolyzers [3].

In this work, we report a new type of OER anodes based on iridium double perovskites (Ir DPs) which contain 32 atom% less iridium and yet exhibit more than 3-fold higher activity per cm2 of electrochemical surface area for OER in acid media compared to IrO_2 benchmarking catalyst [4], with more than 90% Faradaic efficiency. We will show that the OER activity and stability sensitively depends on the crystal structure of the Ir-based catalysts. Moreover, our electrochemical results will provide evidences indicating that a 3D network of corner-shared octahedra is a necessary prerequisite for the catalytic activity enhancement of the iridium-based double perovskites and for their chemical stability under anodic working conditions. We speculate that the superior performance of the Ir DPs is due to the fact that the perovskite-like network may maximize the orbital interaction between the cations and the oxygen anions which may allow to adjust the cations – oxygen distances to accommodate local charge changes. Since the adsorption of the OER intermediates may require the iridium centers to adjust their charges, the breathing mode displacement of oxygen in the perovskite-like network would favor the overall reaction. These lattice adjustments do not exist in the rutile structure (IrO_2) or in fluorite-like compounds and may explain their lower OER activities.

References

[1] Cherevko, S et al. ChemCatChem 2014, 6, 2219.
[2] Danilovic, N et al. J. Phys. Chem. Lett. 2014, 5, 2474.
[3] Turner, J. A. Sustainable Hydrogen Production. Science 305, 972-974.
[4] McCrory, C.C. et al. J. Am. Chem. Soc. 2013, 135, 16977

T29

Effect of ad-atoms on reconstruction of shape-controlled Pt nanoparticles

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The well-defined single crystal electrodes were used as model surfaces to investigate the structure-sensitivity of electro-oxidation of small organic molecules and oxygen reduction reactions (ORR) [1,2,3] because of their profound dependence on surface structure properties; these reactions have immense applications in fuel cells and energy storage devices. Single crystal surfaces are known to undergo reconstruction [3] in the electrochemical environment while in contact with the electrolyte solution or during the potential cycling; it is also influenced by the presence of adsorbates. For bulk catalytic applications, it is imperative to investigate the reconstruction on shape-controlled Pt nanoparticles. However, converting these findings to the bulk catalysts had met with handful of challenges. One such aspect is getting well-cleaned Pt nanoparticles, which is an indispensable prerequisite for any surface-structure analysis. Recently, Vidal-Iglesias et al. investigated the effect of UV/ozone cleaning treatment on shaped-controlled Pt nanoparticles and demonstrated using electrochemical techniques that the cleaning process perturbs the surface structure of the nanoparticle [4]. The resulting surface modification significantly alters the catalytic activity.

Therefore, in this work we employed an in-situ potentiostatic method to remove the surfactants and other organic impurities from the Pt surface without altering the surface-structure. The cleanliness of the Pt surface obtained through this method is confirmed from the voltammetric features recorded in the test electrolyte (0.5 M H2SO4). Also, we investigated reconstruction of shape-controlled Pt nanoparticles in relevance to the ORR. The potential cycling in the region 0.06–1 V and 0.06–1.2 V in H2SO4 electrolyte results in the surface reconstruction and consequent loss of characteristic surfaces of different shape-controlled nanoparticles. Furthermore, the fractional loss of surface faceting is estimated through in-situ irreversible adsorption of bismuth (Bi) and germanium (Ge). Morphological changes are analysed with ex-situ HRTEM. The presence of halide ad-atoms (Cl, Br and I) on the Pt surface results in the attenuation of electro-oxidation of Pt nanoparticles, so was the reconstruction; as the ad-atoms hinder the adsorption of oxygenated spices from the electrolyte on to the Pt surface.

References

[1] N. M. Markovic, H. A. Gasteiger, P. N. Ross, J. Phys. Chem. 99 (1995) 3411–3415.

[2] N. M. Markovic, R. R. Adzic, B. D. Cahan, E. B. Yeager, J. Electroanal. Chem. 377 (1994) 249–259.

[3] R. Devivaraprasad, R. Ramesh, N. Naresh, T. Kar, R. K. Singh and M. Neergat, Langmuir 30 (2014) 8995–9006.

[4] D. M. Kolb, Prog. Surf. Sci. 51 (1996) 109–173.

[5] F. J. Vidal-Iglesias, J. Solla-Gullón, E. Herrero, V. Montiel, A. Aldaz, J. M. Feliu, Electrochem. Commun. 13 (2011) 502–505.

7 New Electrocatalytic Materials

T30 Theoretical and experimental investigations on BN on gold as an efficient electrocatalyst

Kohei Uosaki

T31 Ordered Pt adlayer on Au(111) and its electrocatalytic properties

Shuelin Yau

T32 Application of Rh-containging highly-acidic mixed-metal (W, Zr) oxide films as active supports for noble metal electrocatalytic nanoparticles: enhancement of oxidation of organic fuels

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T33 Enhancement of electrocatalytic activity of carbon-based cathodes for electrochemical wastewater treatment

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T34 Water splitting on illuminated semiconductors

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T35 New core-shell nano-structures (CSNS) for critical energy conversion

Radenka Maric

Chairs: Prof. Marc T.M.Koper and Dr. Kathryn Toghill

T30

Theoretical and Experimental Investigations on BN on Gold as an Efficient Electrocatalyst for oxygen reduction reaction – Importance of BN-Au Interaction –

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Large overpotential for oxygen reduction reaction (ORR) is one of the most serious problems in the development of fuel cells. Although Pt based electrocatalysts are known to be most efficient, they have several problems such as high cost, less abundance, poor stability, and still sluggish kinetics. Many efforts have been made to find alternative catalysts. Recently we theoretically proposed that hexagonal boron nitride (h-BN) monolayer, which has geometric structure similar to the graphene but is an insulator with a wide band gap (5.8eV), can be used as an ORR catalyst [1-3].
In the present study, electrocatalytic activity of BN nanosheets (BNNS) on Au(111) for ORR is investigated both theoretically and experimentally.

DFT calculations for BN/Au(111) predicted the possible ORR activity of BN/Au(111) [4] and electrocatalytic activities of various types of BN, i.e., spin coated BN nanotube (BNNT), BN nanosheet (BNNS) and sputter deposited BN, on Au electrodes as well as those of BNNS modified glassy carbon (GC) and Pt electrodes for ORR were examined [4, 5]. The overpotential for ORR at Au electrode was reduced by ca. 100, ca. 270, and ca.150 mV by spin coating of the dispersion of BNNT and liquid exfoliated BNNS, and sputter deposition of BN, respectively. The reason why the highest activity was obtained by the BNNS modification is attributed to the presence of B-and/or N-edge structures.

While the BN modification was effective to improve ORR activity at Au electrode, it has no and negative effects at GC and Pt electrodes, respectively, suggesting the important role of BN-substrate interaction. One would expect higher ORR activity if we can increase the BN – Au interaction. The interaction was increased by depositing gold nanoclusters (Au-NCs) on BNNS, which was then placed on a Au electrode (Au-BNNS/Au). The decoration of BNNS with gold clusters not only reduced the overpotential for ORR further by ca. 50 mV, but also opened a 4-electron reduction route to water, confirming the important role of Au-BN interaction for ORR [6].

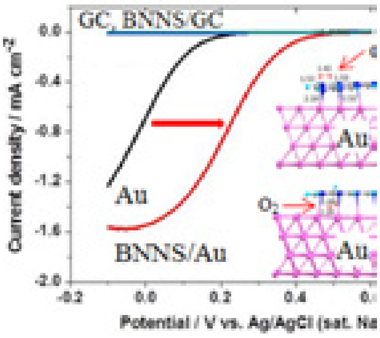

Figure 1. Current-potential relations of bare Au, BNNS/Au, bare GC and BNNS/GC in O2 saturated 0.5 M H2SO4. Optimized structure of the metastable O2 in B-B bridge and B-Au bridge configurations at the edge of h-BN island on Au(111) surface [4].

References

[1] A. Lyalin, A. Nakayama, K. Uosaki, and T. Taketsugu, PCCP, 2013, 15, 2809.
[2] A. Lyalin, A. Nakayama, K. Uosaki, and T. Taketsugu, JPC C, 2013, 117, 21359.
[3] A. Lyalin, A. Nakayama, K. Uosaki, and T. Taketsugu, Top. Cat., 2014, 57, 1032.
[4] K. Uosaki et al., J. Amer. Chem. Soc., 2014, 136, 6542.
[5] G. Elumalai, H. Noguchi, and K. Uosaki, PCCP, 2014, 16, 13755.
[6] G. Elumalai et al., Electrochem. Comm., in press (2016).

T31

Carbon Monoxide Promoted Deposition of Ordered Pt Adlayer on Au(111) and Its Electrocatalytic Properties

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In situ scanning tunneling microscopy (STM) was used to examine the microstructures of platinum (Pt) deposited on ordered Au(111) substrate in aqueous Na2PtCl6 solution saturated with carbon monoxide (CO) with and without potential control at room temperature. PtCl62− complexes were reduced to Pt atoms by CO molecules and deposited on Au(111) in a hexagonal array without potential control. The adsorption of CO molecules first mobilized and rearranged Pt adatoms on Au(111) from disordered Pt aggregates to 0.9 nm wide tortuous stripes, and then to patches of ordered atomic arrays at 0.1 V (versus reversible hydrogen electrode).

Electrodeposition of Pt in the presence of CO ceased with a monatomic Pt film capped with CO molecules arranged in a (2 × 2) array at 0.1 V. The CO monolayer adsorbed on Pt/Au(111) was stripped off at 0.96 V in 0.1 M H2SO4, as compared with 0.83 V observed with Pt(111). The E1/2 potential for oxygen reduction reaction (ORR) observed with the Pt-modified Au(111) electrode was 0.81 V in sulfuric acid, which is 0.16 V more positive than that of Pt(111). The microstructures of the as-prepared Pt monolayer on Au(111) changed with potential cycling between 0.05 and 1.0 V.

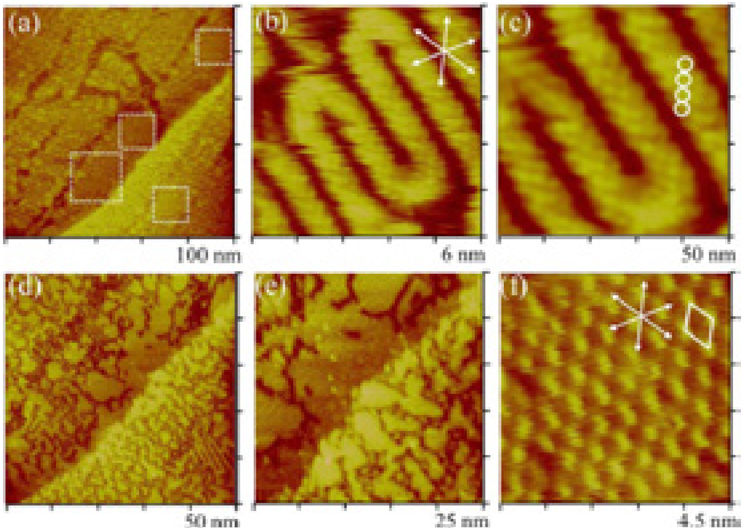

Figure 1. In situ STM images obtained with Pt/Au(111) electrode at 0.1 V in CO-saturated 0.1 M H_2SO_4. Panel (a) was obtained 20 min after CO was added. Torturous chains are highlighted with the dotted squares in panels (b) and (c). Panel (d) shows that the second stage of CO-induced structures imaged as hexagonal arrays □30 nm (e). The molecular structure of the CO adlayer is revealed in panel (f). The bias voltage and setpoint current were 150 mV and 1 nA.

References

[1] Liao W., Liao W., Yau S. J. Electrochem. Soc.162 (2015) H767-773.

T32 Application of Rh-containing highly-acidic mixed-metal (W, Zr) oxide films as active supports for noble metal electrocatalytic nanoparticles: enhancement of oxidation of organic fuels

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Recently, there has been growing interest in development of fuel cells (e.g. utilizing small organic molecules) as alternative technologies to hydrogen based electrochemical energy systems. For example, ethanol (biofuel) can be ideally oxidized to carbon dioxide thus delivering twelve electrons. But realistically the reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of tungsten, titanium or zirconium [1,2]. Also gold in combination with platinum has been demonstrated to produce novel high performance bimetallic catalysts.

We pursue a concept of utilization of mixed metal (e.g. zirconium/tungsten or titanium/tungsten) oxide matrices for supporting and activating noble metal nanoparticles (e.g. PtRu) during electrooxidation of methanol and ethanol. Among important issues is incorporation of Rh nanostructures capable of weakening, or even breaking, the C-C bond in the ethanol molecules. On the other hand, rhodium itself is not directly electrocatalytic toward oxidation of ethanol. The oxides and noble metal nanoparticles have been deposited in a controlled manner using the layer-by-layer method. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites. In addition, formation of “nanoreactors” where ethanol is partitioned (at Rh) to methanolic residues further oxidized at PtRu cannot be excluded.

References

[1] Rutkowska IA, Zoladek S, Kulesza PJ. Electrochim. Acta 162 (2015) 215–223.
[2] Rutkowska IA, Kulesza PJ. J. Electrochem. Soc. 163 (2016) H1-H9.

T33

Enhancement of electrocatalytic activity of carbon-based cathodes for electrochemical wastewater treatment

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Electrochemical advanced oxidation processes (EAOPs) are being developed with the goal to treat hazardous persistent organic pollutants (POP), before they are released into the natural environment. These methods rely on the electrochemical generation of very powerful oxidizing agents – the strongest of which being the hydroxyl radical ($^{\bullet}OH$) – in solution. These agents have the potential to destroy and mineralize organic compounds. Among EAOPs, electro-Fenton – based on the electrogeneration of the Fenton's reagent (H_2O_2 and Fe^{2+}) – has emerged because of its many advantages, including very high degradation and mineralization rates of organic pollutants. In electro-Fenton, the cathode material plays a crucial role by promoting the formation of the Fenton's reagent. Carbon-based cathodes appear to be the most effective due to their high H_2 evolution overpotential and their low electrocatalytic activity for H_2O_2 decomposition. Among carbon materials, graphene displays exceptional properties – such as high electrical conductivity and high specific surface area – which have triggered a graphene gold rush. However, the potential of graphene as electrode material for environmental applications is only starting to be considered.

In this study, graphene-based electrodes were manufactured using an ink-coating technique [1]. Carbon cloth was used as raw material and the quality of the coating was assessed by visual observation as well as by monitoring H_2O_2 production. The electrode physical and structural properties were determined by electrochemical measurements (cyclic voltammetry, impedance spectroscopy and linear sweep voltammetry), microscopy and spectroscopy. Figure 1a depicts the optical micrograph of graphene-coated cloth, highlighting the presence of nanoscale clusters formed by graphene agglomeration. Furthermore, the graphene-coated cloth was able to produce twice as much H_2O_2 as the uncoated one (Figure 1b) demonstrating performance enhancement in the presence of graphene. Such improvement was caused by (i) the enhancement of surface area, which increased the number of active sites on which O_2 could adsorb for its subsequent reduction to H_2O_2 and; (ii) the increase of electrical conductivity of the raw material, which increased the rate of O_2 reduction reaction at the cathode surface. In conclusion, graphene-coated carbon cloth proved to be a suitable cathode for electro-Fenton treatment of wastewater.

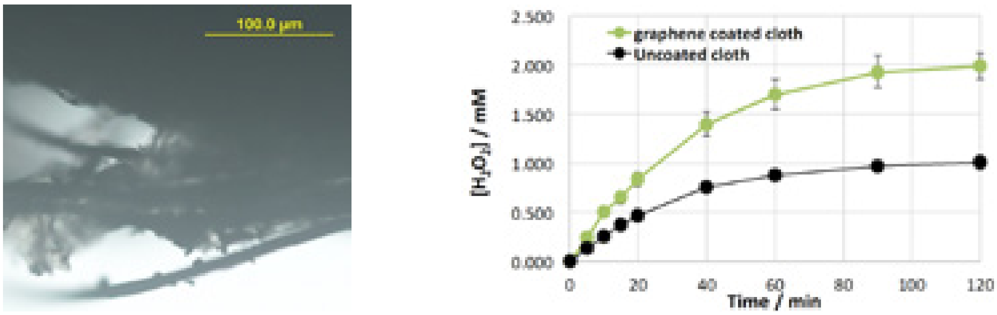

Figure 1. Performance of graphene coating; (a) optical micrograph of graphene-coated carbon cloth, (b) H2O2 electrogeneration performance.

References

[1] Mousset E, Ahmad SM, Wang Z, Lefebvre O Int. Soc. Electrochem Annual Conf. (2015).

T34

Water splitting on illuminated semiconductors – Surface sensitivity of the hydrogen and oxygen evolution on titanium dioxide polymorphs

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Photo-electrochemical water splitting represents one of the key processes needed for successful utilization of renewable energy sources for distributed generation, storage and use of energy.[1] The research related to the electrochemical and photo-electrochemical splitting of water is primarily motivated by electricity storage in hydrogen. The overall process itself, however, is limited by the kinetically sluggish oxygen evolution reaction (OER). Primary effort was therefore focused on a development of new oxygen evolution catalysts based on rational design approach combining the DFT screening with target synthesis. This approach turned out to be quite successful has identifying feasible new oxygen evolution catalysts based on first-row transition-metal oxides (Mn, Fe, Co, Ni) [2, 3] and perovskites [4] matching or surpassing the activity of iridium- and ruthenium oxides.

Surprisingly, the same approach has not yet be implemented for systematic development of the novel (photo)catalysts capable of direct conversion of the radiation energy into energetically useful hydrogen. The application of the rational design approach is hindered by a lack of the fundamental understanding of the electrocatalytic behavior of illuminated semiconductors. The presented paper will, therefore, focus on the hydrogen and oxygen evolution on illuminated TiO_2 (anatase) electrodes. The characteristic surface sensitivity of the catalytic behavior of anatase surfaces will be demonstrated on the nano-particulate materials dominated by {110}, {101} and {001} oriented surfaces. The photo-electrochemical data will be complemented with differential electrochemical mass spectroscopy detection of the reaction products and discussed in terms of the models of the catalytic behavior based on first principle DFT calculations.

References

[1] Lewis NS, Nocera DG Proc. Natl. Acad. Sci. U.S.A, 103 (2006) 15729.
[2] Gorlin Y. et al., J. Am. Chem Soc, 2013, 135, 8525
[3] Lufterman D.A., Sudranath Y., Nocera D.G., J. Am. Chem. Soc. 2009, 131, 3838
[4] Suntivich J., et al., Science 2011, 334, 1383.

T35

New core-shell nano-structures (CSNS) for critical energy conversion

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Catalytic materials are complex systems in which achieving the desired properties (i.e. activity, selectivity and stability) depends on exploiting the many degrees of freedom in: surface and bulk composition, geometry, defects, interactions with the support material, control of the reacting environment. Moreover, the local composition and structure of catalytic systems evolve dynamically over a range of time and length scales, and are often facilitated by the reacting environment, leading to a loss in the desired properties – a major obstacle that industry is looking to address. The active catalyst materials have been synthesized by the Reactive Spray Deposition Process (RSDT). The RSDT process bypasses traditional wet chemical routes by simultaneously nucleating the catalyst on a support and sequential deposition of catalytic layers via gas-phase onto membrane.

Atomically-ordered core-shell nanostructure (CSNS) catalysts are unique because of their tunable physical and chemical properties through bulk and surface chemistry, relative sizes of the core and shell, defects, catalyst support, etc. Pt-monolayer core/shell catalysts with low or zero precious metal content in the cores provide the most promising approach to simultaneously achieving the high mass-specific activity, adequate durability, and the high Pt surface area apparently needed to achieve good performance at high current densities in air. The new class of CSNS structure is created of ordered intermetallic metals as cores with a monolayer of Pt. This is a new class of ordered intermetallic compounds having high stability and activity for the oxygen reduction reaction, ORR. The structure of the core particle of Pd:Ru made by RSDT is shown in Figure.1 Pd and Ru are atomically mixed and no phase segregation was observed. There is no evidence of the oxides for either phase.The Pt monolayer has been deposited after the core is formed. Enhancement in ORR was observed.

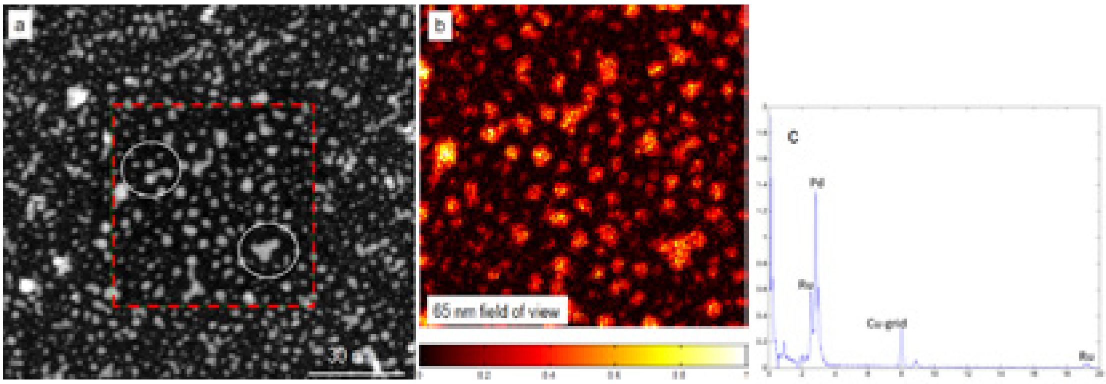

Figure 1. HAADF images demonstrating A) the uniformity of the film during early stage growth, B) mapping, and C) the multivariate statistical analysis of the XEDS signal.

8 Fundamental Electrochemistry

T36	Equilibrium adsorbate structures at electrochemical electrode/electrolyte interfaces studied from first principles	*Axel Groß*
T37	The impact of high-frequency-high-current perturbations	*Kotub Uddin*
T38	Best practices fo electrochemical test methods	*Rob Sides*
T39	Electronic excitation induced by confined electromagnetic field at electrified interfaces	*Kei Murakoshi*
T40	STM studies in ionic liquids of electrochemical single molecule transistors and molecular wres	*Richard J. Nichols*
T41	Gaining insights into Au | Room temperature ionic liquids interfaces through the study of adsorption phenomena	*Thomas Doneux*

Chairs: Prof. Hubert Girault and Prof. Takamasa Sagara

T36 Equilbrium adsorbate structures at electrochemical electrode/electrolyte interfaces studied from first principles

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The reliable theoretical modeling of processes occurring at electrochemical interfaces requires an appropriate description of the atomistic structure of the interface. In particular, the correct coverage of specifically adsorbed ions needs to be taken into account as they considerably modify the electronic properties of the electrode. Recently, we have determined the coverage of halides on metal electrodes by coupling periodic density functional theory (DFT) calculations with a grand-canonical description of the electrolyte [1]. Here we will present an extension of this approach by considering the co-adsorption on hydrogen and halides on Pt(111). We will demonstrate that hydrogen and halide adsorption is competitive, i.e., upon increasing the electrode adsorption adsorbed hydrogen is replace by halides, in agreement with experimental findings.

In these calculations, the influence of the presence of the electrolyte on the adsorption energies is neglected. Still, its presence might significantly modify the stability of specifically adsorbed species and of reaction intermediates and barriers in electro-catalysis. Representing the electrolyte by an implicit solvent model is computationally very attractive and yields reasonable results with respect to adsorbate coverage of Pt(111) as a function of electrode potential [2]. We will show that this approach also reproduces the correct selectivity in methanol electro-oxidation on Pt(111). At the same time, we are trying to figure out how many explicit water layers are needed in order to give a correct description of the interface between Pt(111) and an aqueous electrolyte. Based on the results of ab initio molecular dynamics simulations, we find that six water layers are apparently sufficient to properly reproduce the structural features of the aqueous electrolyte at the interface and to give the correct potential of zero charge.

References

[1] Gossenberger F, Roman T, Groß A Surf. Sci. 631 (2015) 17-22.

[2] Sakong S, Naderian M, Mathew K, Hennig RG, Groß A J. Chem. Phys. 142 (2015) 234107.

T37

The impact of high-frequency-high-current perturbations on ion dynamics around the negative electrode-electrolyte interface

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In application, bidirectional Lithium ion battery chargers draw sinusoidal current in both charge and discharge modes. The trace of the current waveform during charging of a Nissan Leaf vehcile using a 3kW Eltek Valere charger and the harmonic content is presented in Figure 1.

In recent work, the authors have shown that exposing the battery to such coupled direct current (dc) and alternating currents (ac) lead to additional battery degradation over what is attributed to a pure dc load [1]. From analysis of electrochemical impedance spectroscopy data, it is suggested that this additional degradation materializes through the growth of the solid electrolyte interface on the carbon/electrolyte interface.

It is known that cell impedance is frequency dependent; consequently heat generation within the battery will be a function of excitation frequency. This frequency dependent impedance may be attributed to the transference number – defined as a contribution of ion species to a total current flow – being less than 1 at small timescales [2]. Under a typical dc load, a portion of the anions carry the current until a steady state diffusion gradient is established. If the system is constantly being perturbed (with an ac ripple current) however, a state of equilibrium is never achieved and there is persistent ion flux around the carbon/electrolyte interface.

In this paper, the underlying causality of degradation caused by coupled dc-ac current is studied by employing extensions of electrochemical models, such as those described in Ref. [3].

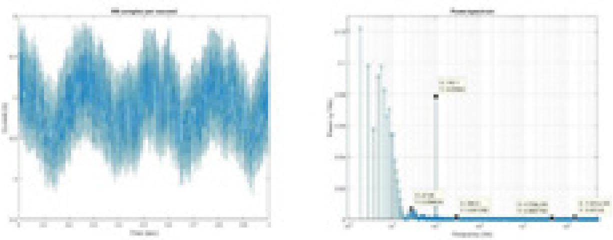

Figure 1: The left hand panel shows the measurement of a coupled dc-ac current. The scope settings were: 100ms per division, with 106 samples taken per second. The right hand panel is the power spectrum of the measured current.

References

[1] Uddin K, et. al., Applied Energy (in the press).
[2] Xiao M, Choe S-Y, Journal of Power Sources, 277 (2015) 403-415.
[3] Wang H, Varghese J, Pilon L, Electrochimica Acta, 56 (2011) 6189-6197.

T38

Best Practices of Electrochemical Test Methods for Energy-Storage and Energy-Conversion Devices including Li-Ion Batteries

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A tremendous industrial and consumer need exists for a portable rechargeable (secondary) energy source that has a high-capacity; can function at high-discharge rates, thus delivering pulse-power; and a sufficient cycle life. Since the early 1990s, Li-ion batteries have been the best technology available due to their intrinsic energy density.

The success of the original Li-based energy storage device technology spawned research by chemists, material scientists and computational scientists for improved anode materials, cathode materials, and electrolytes. Engineers have worked diligently to advance thermal management, packaging, production methods to make smaller, cheaper, faster, and safer devices.

Potentiostats have played an integral role in the research, development, and production of energy devices. Electrochemical tests can range from cyclic voltammetry, constant-current discharge tests or EIS for the evaluation of the cycle-life of complete cells. With scientists from a variety of backgrounds working in this field, specific tests have been created to benchmark key characteristics and from these best practices have evolved.

Join Dr. Rob Sides of AMETEK - Princeton Applied Research and Solartron Analytical for a presentation that addresses practices for the importance of DC accuracy in all techniques; Electrochemical Impedance Spectroscopy (EIS) tests, including the comparison of Galvanostatic EIS and Potentiostatic EIS; and the value of auxiliary measurements to Anode/Cathode or stack-testing.

These concepts are applicable for all generations of testing: half-cell tests for material development; single complete cell; and stacks. The importance of capacitors and fuel cells as parts of the solution for portable power will also be discussed.
Advanced understanding of the electrochemical measurement system – the potentiostat, the cable, and the software – should allow improved experimental design and confidence in test results.

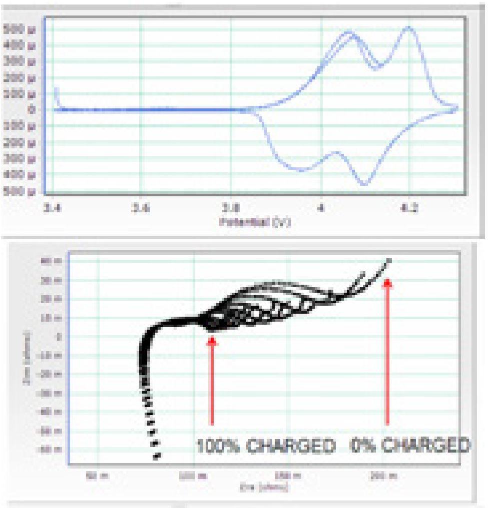

Figure 1 – Typical electrochemical test data generated from a potentiostat to evaluate Li-ion battery key characteristics.

Figure 2 – A multichannel potentiostat used to generate data, such as those presented in Fig. 1.

T39

Electronic Excitation induced by Confined Electromagnetic Filed at Electrified Interfaces

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Excitation of localized surface plasmon resonance (LSPR), which is the resonant collective oscillation of free electrons in metals, leads to the effective formation of excited states in nanomaterials. The excited states promote surface chemical reactions. After the 1981 report of an innovative theoretical proposal of efficient photochemistry induced on rough metal surfaces by the interaction between adsorbed molecules and a localized plasmon [1], various experimental approaches have proved the validity of LSPR-enhanced chemical reactions, such as metal depositions, molecule oxidation/reduction, and the formation of chemical bonds, etc. We also developed the system for photoenergy conversions as well as molecule manipulation [2]. In these systems, very unique excitation process becomes available because of the confined electromagnetic fields comparable with the size of exciton in electronic band structures of materials. In the presentation, possibilities of the application based on the LSPR excitation for effective electron transfer reactions at electrified interfaces will be discussed.

References

[1] Nitzan, A., Brus, L. E. J. Chem. Phys. 75 (1981) 2205-2214; Nitzan, A., Brus, L. E. J. Chem. Phys. 74 (1981) 5321-5322.

[2] Li, X., Suzuki, K., Toda, T., Yasuda, S., Murakoshi, K., J Phys Chem C 119 (2015) 22092-22101; Nagasawa, F., Takase, M., Murakoshi, K., J. Phys. Chem. Lett., 5 (2014) 14-19; Takase, M., Ajiki, H., Mizumoto, Y., Komeda, K., Nara, M., Nabika, H., Yasuda, S., Ishihara, H., Murakoshi, K., Nature Photonics 7 (2013) 550-554.

T40

STM Studies in Ionic Liquids of Electrochemical Single Molecule Transistors and Molecular Wires

Richard J. Nichols1, and Osorio, H. M.; Cea, P.; Gluyas, J. B. G.; Hartl, F.; Higgins, S. J.; Leary, E.; Low, P. J.; Martín, S.; Tory, J.; Ulstrup, J.; Vezzoli, A.; Milan, D. C.; Zeng, Q.; Catarelli, S. R.; Schwarzacher, W.; Mao, B.-W.; Yan, J.-W.; Jeppesen, J. O.; Lycoops, J; Kay, N. J.; Haiss, W. and Sedghi, G.*
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We have exploited STM based methods for making single molecule measurements under electrochemical potential control in ionic liquid electrolytes.[1-4] The electrochemical potential can be used to control the redox state of single molecule bridges and switch the electrical conductance from low to higher values. This has been referred to as the "single molecule electrochemical transistor" configuration, with the electrochemical potential "gating" the molecular conductance in the STM nano-gap configuration. Recent results from our group on gating the conductance of single molecules in ionic liquid electrolytes will be discussed including studies of viologens, redox active metal terpyridine molecular wires and pyrrolo-tetrathiafulvalene (pTTF) molecular bridges. Mechanisms of charge transport in the STM nano-gap setup are discussed alongside the advantages of undertaking such single molecule electrochemical measurements in ionic liquids.

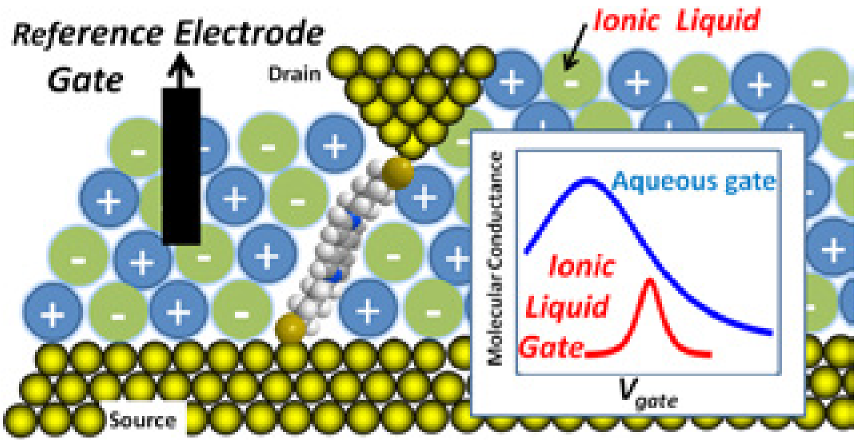

Figure 1. Electrochemical single molecule gating examined in ionic liquid electrolytes using an electrochemical STM with bipotentiostat control of the electrochemical potential of the substrate and STM tip.[1]

References

[1] Osorio, H. M.; Catarelli, S.; Cea, P.; Gluyas, J. B. G.; Hartl, F.; Higgins, S. J.; Leary, E.; Low, P. J.; Martín, S.; Nichols, R. J.; Tory, J.; Ulstrup, J.; Vezzoli, A.; Milan, D. C.; Zeng, Q. Electrochemical Single-Molecule Transistors with Optimized Gate Coupling. Journal of the American Chemical Society 2015, 137, 14319-14328.
[2] Catarelli, S. R.; Higgins, S. J.; Schwarzacher, W.; Mao, B.-W.; Yan, J.-W.; Nichols, R. J. Ionic Liquid Based Approach for Single-Molecule Electronics with Cobalt Contacts. Langmuir 2014, 30, 14329-14336.
[3] Kay, N. J.; Higgins, S. J.; Jeppesen, J. O.; Leary, E.; Lycoops, J.; Ulstrup, J.; Nichols, R. J. Single-Molecule Electrochemical Gating in Ionic Liquids. Journal of the American Chemical Society 2012, 134, 16817-16826.
[4] Kay, N. J.; Nichols, R. J.; Higgins, S. J.; Haiss, W.; Sedghi, G.; Schwarzacher, W.; Mao, B.-W. Ionic Liquids As a Medium for STM-Based Single Molecule Conductance Determination: An Exploration Employing Alkanedithiols. Journal of Physical Chemistry C 2011, 115, 21402-21408.

T41

Gaining insights into Au | Room Temperature Ionic Liquids interfaces through the study of adsorption phenomena

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Room temperature ionic liquids (RTILs) have received in the last decade a tremendous attention, because their unique physical properties make them promising for a range of novel electrochemical devices. From a fundamental perspective in interfacial electrochemistry, RTILs are exciting, non-conventional electrolytes, since their description departs from well-established double-layer theories. The interpretation of voltammetric or impedimetric features recorded at bare metal|RTIL interfaces is notoriously difficult.

While the traditional approach consists in the acquisition of data characteristic of the electrode in contact with a pure RTIL, we propose to get information on the interfacial behaviour of the RTILs through competitive adsorption phenomena to modify drastically the structure of the interface and make the interpretation of electrochemical data easier. Adsorption at metal electrodes is a complex process governed by various interactions involving the surfactant, the electrode and the electrolyte. In particular, besides the interactions taking place in the bulk, the surfactant-electrode and the electrolyte-electrode interactions are of most importance. In this communication, we present the results obtained in imidazolium-based RTILs where the anion was either dicyanamide (DCA) or bis(trifluoromethanesulfonyl)imide (NTf_2). Experiments were carried out in a nitrogen controlled atmosphere in a glove-box, using both polycrystalline and single-crystal gold electrodes. Bipyridine and 2 thiouracil were chosen as representative compounds undergoing physisorption and chemisorption, respectively, on gold substrates. The overall behaviour of 2 thiouracil is reminiscent of that observed in conventional solvents for thiols self-assembled on gold. Spontaneous adsorption is evidenced, and the adsorbate can be removed from the surface through a reductive desorption process. The strong adsorption of 2 thiouracil is further evidenced by its significant inhibition of the cathodic deposition of copper, and by comparison with the behaviour of uracil.

9 Nanostructures and Nanomaterials

T42 Nano-gap structures for surface spectroscopy, energy conversion and nanofabrication

Katsuyoshi Ikeda

T43 Nanometer-thick gold on silicon as a proxy for single-crystal gold for the electrodeposition

Jay A. Switzer

T44 Controlled synthesis and characterization of unprotected nanoparticles

Jonathan Quinson

Chairs: Prof. Frédéric Maillard

T42

Nano-gap structures for surface spectroscopy, energy conversion, and nanofabrication

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Nanostructured metals often exhibit unique physical properties. For example, the optical property of noble metals is significantly affected by size and shape of the nanostructures due to the appearance of surface plasmon resonances. The electrochemical behavior of nanostructured metal electrodes may be different from that of flat metal surfaces because mass transfer or electrochemical double layer is affected by the nanostructured surface features. Here, sphere-plane type nano-gap structures are formed on molecular monolayer-covered metal electrodes with atomically defined interface structures by adsorption of Au nanoparticles. Since these nano-gaps can confine incident photon energy at the nanoscale, the efficiency of surface enhanced Raman scattering is greatly enhanced in the gaps [1-4]. Vibrational spectroscopic studies of atomically defined metal-molecule model interfaces is conducted using this system. When a metal surface is covered with chromophores, uphill electron transfers can be induced through photo-excitation of the chromophores. The efficiency of this photo-induced uphill electron transfer is enhanced by forming the nano-gaps because they function as optical antennae [5, 6]. Moreover, nanofabrication of molecular monolayers is also possible by the use of the nano-gaps. Since the formation of the nano-gap structures locally stabilize molecular layers, reductive desorption of thiol monolayers in the presence of the nano-gaps results in formation of molecular nanodot structures [7]. Electrochemical behavior of two-component molecular assembly is compared with and without nanoscale surface features.

References

[1] Hu J, Hoshi N, Uosaki K, Ikeda K. Nano Lett. 15 (2015) 7982-7986.

[2] Hu J, Tanabe M, Sato J, Uosaki K, Ikeda K. J. Am. Chem. Soc. 136 (2014) 10299-10307.

[3] Ikeda K, Suzuki S, Uosaki K. J. Am. Chem. Soc. 135 (2013) 17387–17392.

[4] Ikeda K, Suzuki S, Uosaki K. Nano Lett. 11 (2011) 1716-1722.

[5] Ikeda K, Takahashi K, Masuda T, Kobori H, Kanehara M, Teranishi T, Uosaki K. J. Phys. Chem. C. 116 (2012) 20806-20811.

[6] Ikeda K, Takahashi K, Masuda T,Uosaki K. Angew. Chem. Int. Ed. 50 (2011) 1280-1284.

[7] Ikeda K, Takeuchi Y, Kanamaru K, Suzuki S,Uosaki K. J. Phys. Chem. C. DOI: 10.1021/acs.jpcc.5b11691.

T43 Nanometer-thick gold on silicon as a proxy for single-crystal gold for the electrodeposition of epitaxial ceramic thin films

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Gold metal is a favorite electrode for electrochemical studies due to its chemical inertness. Single-crystal Au has also been used extensively as a substrate for the electrodeposition of thin layers of metals by underpotential deposition and as a substrate for epitaxial growth of semiconductors. Our group has been involved with the epitaxial electrodeposition of thin films and superlattices of metal oxides for many years [1,2]. Although single-crystal Au does provide a platform for studies of the basic science behind epitaxial electrodeposition, there is little (or, perhaps, zero) probability that these epitaxial systems will be technologically exploited, due to the high cost and small size of Au single crystals. Allongue and co-workers introduced an electrochemical method to grow thin, ultraflat Au(111) epitaxial buffer layers on hydrogen terminated Si(111) [3]. Here, we show that epitaxial Cu_2O films can be electrodeposited onto Si(111), Si(100), and Si(110) wafers that have been electrodeposited with a thin layer of epitaxial Au. In all cases, the Cu2O films have both out-of-plane and in-plane orientations that are determined by the Si/Au substrates. The Au film thicknesses were determined by X-ray reflectivity and Laue oscillations, and the orientations of the Cu2O epitaxial layers were determined by X-ray pole figures. The highest quality Au and Cu2O films were deposited onto Si(111). The films on Si(100) and Si(110) were highly oriented but they were also twinned. The twinning manifests itself as minor [221] orientations on Si(100) and minor [411] orientations on Si(110).

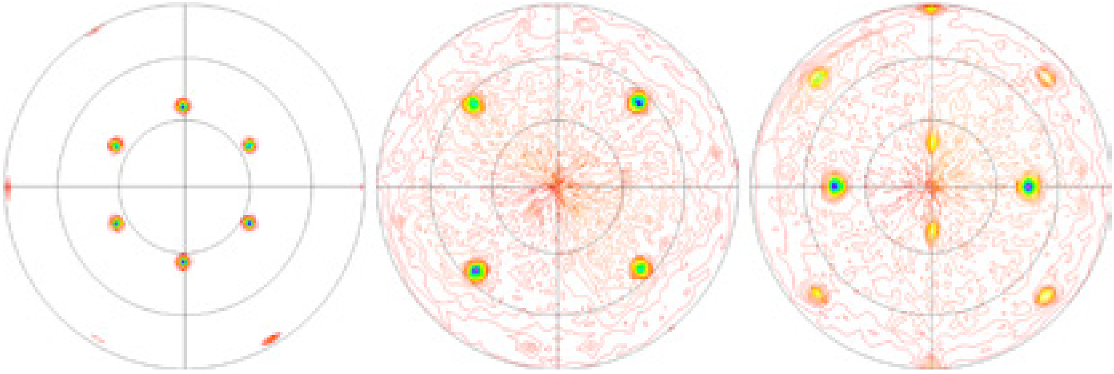

Figure 1. X-ray pole figures of Cu_2O on Au-coated Si(111) (left), Si(100) (middle) and Si(110) (right).

References

[1] Bohannan EW, Shumsky MG, Switzer JA. Chem. Mater. 11 (1999) 2289-2291.
[2] Liu R, Vertegel AA, Bohannan EW, Sorenson TA, Switzer, JA. Chem. Mater. 13 (2001) 508-512.
[3] Prod’homme P, Maroun F. Cortes R, Allongue P. Appl Phys Lett 93 (2008) 171901.

T44

Controlled Synthesis and Characterization of Unprotected Nanoparticles for Electrochemical Applications

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To improve energy conversion in devices like fuels cells, to develop electrocatalytic methods to produce chemicals or to get a deeper fundamental understanding of the electrochemical activity of catalysts, a common requirement is to control the properties of the electrocatalyst used. For instance, different properties like diameter, size distribution or loading of platinum nanoparticles (NPs) on electrodes can affect the efficiency of fuel cells [1]. These properties can now be controlled at the nanoscale by controlled synthesis of the NPs.

To be relevant for electrochemical applications, avoiding the use of undesirable additives or surfactants is a strong advantage because these additives can possibly impair the electrochemical activity. In this regard, the polyol method is a suitable route to develop ‘unprotected’ electrocatalysts and platinum NPs in particular [2].

This talk reviews our recent progress in the controlled synthesis and characterisation of ‘unprotected’ nanoparticles. Challenges that are still to address are also highlighted. It is unlikely that completely ‘unprotected’ NPs will be stable in colloidal suspension, a recent focus has been to establish and control what stabilises these particles [3]. CO groups were found to play a key role in this sense and their density can be controlled during synthesis to some extent.
The particles obtained by the polyol method have already been used in a range of catalytic applications. A specific focus is given in this talk to their applications in electrochemistry and development of high surface area electrodes [2].

References

[1] Nesselberger, M. et al. The effect of particle proximity on the oxygen reduction rate of size-selected platinum clusters. Nat. Mater. 12, 919–24 (2013).

[2] Morsbach, E. et al. Stabilizing catalytically active nanoparticles by ligand linking: Toward three-dimensional networks with high catalytic surface area. Langmuir 30, 5564–5573 (2014).

[3] Schrader, I. et al. Surface Chemistry of ‘Unprotected’ Nanoparticles: A Spectroscopic Investigation on Colloidal Particles. J. Phys. Chem. C 119, 17655–17661 (2015).

10 Batteries

T45

Redox flow lithium batteries based on the redox targeting reactions between ferrocene derivatives and $LiFePO_4$

Hyacinthe Randriamahazaka

T46

In-situ GC/MS studies in gas evolution of Li-rich high-voltage cathode materialof lithium ion battery

Fu-Ming Wang

T47

Lithium oxygen cells as function generators:from declining logarithms to sine socillations

Harry Hoster

Chairs: Prof. Daniel A. Scheron

T45

Redox Flow Lithium Batter based on the Redox Targeting Reactions between Ferrocene Derivatives and LiFePO4

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Redox flow battery (RFB) is considered as one of the most promising large-scale energy storage technologies due to the decoupled energy storage and power output, flexible design and long cycle life. Non-aqueous RFBs, while far less developed than aqueous RFB, possess significant benefits over the former, such as wider electrochemical window and consequently greater energy density. However, the low solubility of redox species in non-aqueous electrolyte presents as a major obstacle for the development of viable non-aqueous RFB. In this regard, a novel device — redox flow lithium battery (RFLB) has recently been developed by us to tackle the above issues.1 In a RFLB, energy is stored in the solid Li-storage materials, which are kept in two separate tanks, while power is released in the electrochemical cell when the redox mediators in electrolytes are circulated through the storage tanks and regenerated via reversible chemical delithiation and lithiation of the materials (Figure 1). There have been several redox systems investigated for RFLB. Here we report a novel functional ionic ferrocene derivative, 1-ferrocenylmethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amine (FcIL) and its application for the cathodic half cell of redox flow lithium battery. The FcIL has excellent solubility and tunable redox potential in different solvent. I has a potential of 3.40 V (vs. Li/Li^+) in carbonate, while 3.60 V in TEGDME based electrolyte. When paired with dibromoferrocene (FcBr2), these two redox mediators in LP40 could reversibly delithiate $LiFePO_4$ during charging process and lithiate $FePO_4$ during discharging process. A RFLB half cell was built based upon the above molecules and material. The redox targeting reactions of the molecules with $LiFePO_4$ greatly extend the capacity of the cell and lead to unprecedently high energy density. The authors acknowledge the support from USPC-NUS Joint Research Program.

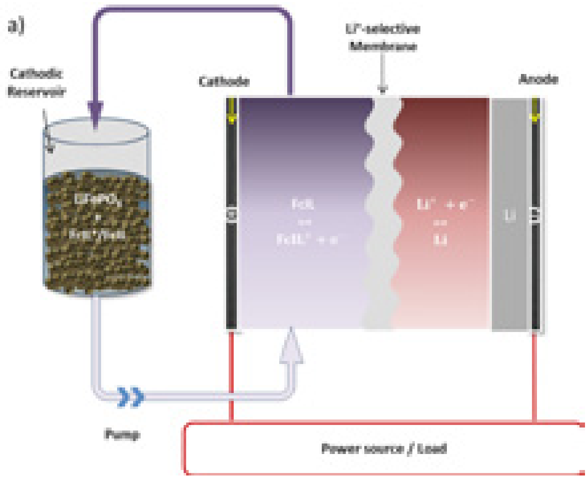

Figure 1. Schematic of the redox flow lithium battery half cell with $LiFePO_4$ kept in a separate tank as the cathodic Li^+ storage material.

References

[1] Q. Huang et al. Phys. Chem. Chem. Phys. 15 (2013) 1793-1797.
[2] C. Jia et al. Sci. Adv. 1 (2015) e1500886.

T46

In-situ GC/MS studies in gas evolution of Li-rich high voltage cathode material of lithium ion battery

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In the presence of literatures, high-voltage (> 4.8V; 5V class) Li-rich layer compounds ($Li[Ni_xLi_{(1-2x)}/3Mn_{(2-x)/3}]O_2$) have been reported to the next candidate of cathode materials in order to increase the power and energy density instead of conventional materials of $LiCoO_2$ or $LiNi_xMn_yCo_zO_2$. These high-voltage Li-rich layer materials dedicate their high reversible capacities more than 270 mAh g^{-1},which is almost twice as higher as $LiCoO_2$ [1-3]. However, this material suffers significantly from problems. Mantia et al. [1] have demonstrated direct evidence of oxygen evolution from the Li-excess material at high potentials by in situ differential electrochemical mass spectrometry (DEMS) as well as Hy et al. [2], who have shown that oxygen activation occurs following electrochemical reaction and forms an irreversible formation of Li_2O, by surface enhanced Raman spectroscopy (SERS). In Jiang's result [3], they are unable to detect any oxygen in their ex situ observation. Their XRD pattern and ^6Li MAS NMR spectrum comment O_2- loss is accompanied with the electrolyte to form CO_2.

In our novel in-situ gas evolution experiment, we showed that there are two reaction mechanisms in the first charge process in Figure 1. In the first reaction mechanism, the CO_2 (m/z 44) and CO (m/z 28) generate drastically at the potential of 4.25V. In comparison with cyclic voltammogram (CV) (not shown in here), the potential of 4.25V is indicated to the reaction of Ni^{3+}/Ni^{4+}; therefore, the gas evolution at this stage can be concluded the electrolyte is partially decomposed with the catalyst of Ni^{3+}/Ni^{4+} and the oxygen evolution is not correlated. Second reaction mechanism starts at 4.65V, the CO_2 forms solely in accompanied with oxygen evolution (m/z 32) from cathode material. Above result indicates that the second reaction mechanism is lead by the oxygen evolution and further reacts with electrolyte.

In this research, we establish a novel in-situ observation for evaluating gas evolution and define the reaction mechanisms of high voltage cathode material.

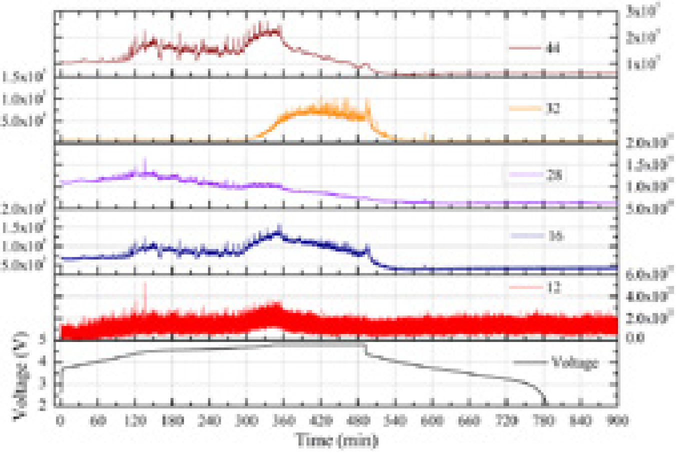

Figure 1. In-situ electrochemical mass

References

[1] F. La Mantia, F. Rosciano, N. Tran, P. Novak, J. Appl. Electrochem. 38 (2008) 893.

[2] Sunny Hy, Felix, John Rick, Wei-Nien Su, Bing Joe Hwang, J. Am. Chem. Soc. 136 (2014) 999.

[3] Meng Jiang, Baris Key, Ying S. Meng, and Clare P. Grey,Chem. Mater. 21 (2009) 2733.

T47

Lithium Oxygen cells as function Generators: from Declining Logarithms to Sine Oscillations

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Their high theoretical gravimetric energy density makes metal-oxygen systems such as lithium-oxygen (Li-O_2) promising candidates for the next generation of rechargeable batteries for mobile applications [1-3]. Li-O_2 cells gain energy from the spontaneous reaction $2\,Li+O_2 \rightarrow Li_2O_2\,(s)$ (Figure 1). That reaction seizes when either all voids in the porous (carbon) cathode are filled, or when the initial electrochemical reaction step is hindered by the growing Li_2O_2 film [2]. Large capacities are achieved when Li_2O_2 forms compact 3D crystals rather than flat 2D films [3]. We have recently demonstrated that the characteristic fingerprint of a given cell, the voltage-vs.-charge profile for constant-current discharged, is essentially the sum of two logarithm curves of opposite orientation (Figure 1) [4]. They can be rationalized by the Nernst and the Tafel equation, which describe the effects of initial superoxide accumulation due to nucleation phenomena and the overgrowth of the electrochemically active surface area by the growing crystallites, respectively. This approach not only explains the initial voltage dip frequently observed for Li-O_2 discharge, but also the 2-stage oscillation behavior that can be observed for graphite cathodes in combination with DME electrolyte (see Figure 2). Key elements are the interface energy between Li_2O_2 and basal vs. edge face carbon and the solubility of LiO_2 in the DME based electrolyte, which is rather sensitive on water and other impurities [3].

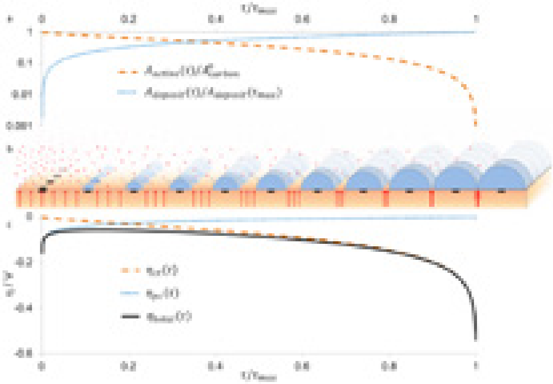

Figure 1. Modelling the voltage profile during constant-current discharge of a Li-O2 cell. Top: increase of Li_2O_2 surface area (blue shapes, dotted curve) and decrease of electrochemically active surface area (dashed curve) Bottom: resulting discharge voltage profile.

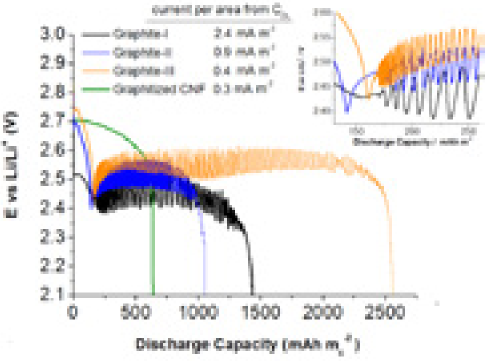

Figure 2. Constant-current discharge profiles for different types of carbon. Graphitic carbon with higher discharge capacity per surface area as compared to carbon nanofibers. Voltage oscillations reflect periodic build-up and removal of passivating films on the electrode, in parallel to solution-pathway build-up of toroidal Li2O2.

References

[1] K.M. Abraham and Z. Jiang, J. Electrochem. Soc. 143 (1996) 1.
[2] J. Højberg et al., ACS Appl. Mater. Interfaces (2015) 4039.
[3] N.P. Aetukuri et al., Nature Chemistry 7 (2015) 50.
[4] A. Rinaldi, O. Wijaya, H.E. Hoster, ChemElectroChem, doi:10.1002/celc.201600184

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KOH activation of coffee grounds: Effect of electrochemical behavior on lithium sulfur battery.

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Lithium-sulfur (Li-S) battery have received attention as the next generation energy devices due to their theoretical specific capacity (1672 mA h g-1) and energy density (2600 W h kg-1).[1] In addition, sulfur has the merits of natural abundance, environmentally material and low cost. Although the Li-S battery has these advantages, its development is faced with several challenges. One of the biggest problems with lithium-sulfur battery is the cycling performance.[2] In this study, carbon pore size was adjusted by KOH activation. The activated carbon-sulfur composite was prepared by a melt-diffusion method. The activated carbon-sulfur composite applied in the preparation of cathode for lithium-sulfur battery. Electrochemical performances of activated carbon-sulfur composite were investigated by a cycling voltammetry (CV), galvanostatic charge/discharge, cycle performance and impedance spectroscopy (EIS).

References

[1] J.W. Kim, J.D. Ocon, D. W. Park, J. Lee. ChemsusChem. 7. (2014) 1265-1273.
[2] X. L. Ji, K. T. Lee, L. F. Nazar. Nat. Mater. 8. (2009) 500-506

P02 Doping effects of electrolyte-electrode interfacial stabilities on Li7La3Zr2O12 garnet-type solid electrolytes

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The fast lithium ion conducting solid electrolytes have been studied extensively due to safety issues of lithium ion batteries. Although many lithium ion conductive materials have been identified, including oxides, sulfides, inorganic glasses and polymers, garnet-type solid electrolyte is considered to be one of the most promising materials for application because of their high lithium ionic conductivity, large potential window and high interfacial stability to lithium metal [1]. In 2003, garnet-type electrolytes of $Li_5La_3M_2O_{12}$ (M = Nb, Ta) were reported but their ionic conductivities were around 10^{-6} S cm^{-1} at 25 ºC [2]. The $Li_7La_3Zr_2O_{12}$ (LLZO) garnet-type solid electrolyte was discovered by Murugan et al. in 2007 and exhibited a high ion conductivity around 4×10^{-4} S cm^{-1} at 25 ºC with electrochemical stability with lithium metal [3]. Of late, many researches have been devoted to apply LLZO to solid-state batteries, but the solid-solid interfacial problems hinder battery performances. In this study, we suggest trivalent (Ga) and pentavalent (Ta) doping effect on the nominal $Li_{7-3x}Al_xLa_3Zr_2O_{12}$ for interfacial compatibility onto electrodes. The tri- and pentavalent dopants can not only help cubic phase formation for high ionic conductivity of nominal LLZO, but also stabilize interfacial contact between electrolyte and electrode. Because the interfacial problems such as resistance and stability were big problems on solid-state batteries, electrochemical analysis of dopants effect on nominal LLZO was characterized.

References

[1] Matsuda Y, Sakamoto K, Matsui M, Yamamoto O, Takeda Y, Imanishi N. Solid State Ionics 277 (2015) 23–29.

[2] Thangadurai V, Kaack H, Weppner W. J. Am. Ceram. Soc. 86 (2003) 437–440.

[3] Murugan R, Yhangadurai V, Weppner W. Angew. Chem. Int. Ed. 46 (2007) 7778 –7781.

[4] Cheng L, Wu CH, Jarry A, Chen W, Ye Y, Zhu J, Kostecki R, Persson K, Huo J, Salmeron M, Chen G, Doeff M. ACS Appl. Mater. Interfaces 7 (2015) 17649–17655.

P03

NEW STOBA technology in lithium ion battery

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Self-Terminated Oligomers Branched Architecture, the STOBA, is used to a surface coating on cathode materials in lithium ion battery (LIB) [1]. As was reported that STOBA is quantified for the increment of battery safety and reaction reversibility due to the high reaction rate of thermal polymerization and high ionic diffusivity of product [2]. In this work, $LiAl_{0.05}Co_{0.95}O_2$ has been choosing to coat with new STOBA, that is modified with 3-Aminopropyltriethoxysilane (APTES) and conventional STOBA. The coupling agent (APTES) in this research is able to enhance the thermal stability of conventional STOBA. Moreover, the Epoxy Acrylate is also used to instead of N,N'-4,4'-diphenylmethane-bismaleimide (BMI) on new STOBA in which combines with Barbituric Acid (BTA) (1:1 mol/mol).
Extensive research has shown that the new STOBA improves the energy density and safety performance when added 5 wt% of solid content to the cathode electrode. This research confirms battery test, differential scanning calorimetry (DSC) and field emission scanning electron microscopy (FE-SEM) that the new STOBA is the next candidate to the safety of LIB.

References

[1] C. C. Lin, H. C Wu, J. P. Pan, C. Y. Su, T. H. Wang, H. S. Sheu, N. L. Wu. Electrochimica Acta 101 (2013) 11– 17

[2] F. M. Wang, S. C. Lo, C. S. Cheng, J. H. Chen, B. J. Hwang, H. C. Wu, J. Membrane Sci. 368 (2011) 165.

[3] Q. T. Pham, J. M. Hsu, J. P. Pan, T. H. Wang, C. S. Chern. Wileyonlinelibrary.com. DOI 10. 1002/pi. 4390

P04

The Development of New Chemistries as Redox Active Electrolytes for Non-Aqueous Redox-Flow Batteries

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Currently, the majority of global energy production is sourced from the combustion of fossil fuels such as coal. However, due to the finite and polluting nature of these resources, their usage must be decreased and instead, renewable resources such as wind power are needed to supplement and diversify energy production. Unfortunately, as these resources are intermittent and too unreliable to depend upon alone, efficient grid-scale energy storage systems must first be implemented before a truly green future can become a reality.
Redox-flow batteries (RFBs) store complimentary redox electrolytes in separate storage tanks which are continuously cycled through an energy converter to source power. However, RFBs are reversible systems which offer long lifetimes, high energy efficiencies and cheap maintenance costs due to their simple and modular design [1]. Furthermore, RFBs are versatile devices which allow independent scaling of power and capacity through the use of liquid electrolytes and simple electrode reactions. Hence, RFBs are uniquely equipped for grid-scale storage, load levelling and power management of renewable energies.
Aqueous RFBs, such as the all-vanadium system, have been successfully commercialized and produce energy densities up to 33Wh/L and efficiencies up to 85% [2]. However, the energy density of aqueous systems is fundamentally limited by the narrow electrochemical window of water and the requirement for high electrolyte concentrations. Therefore, higher energy densities are theoretically achievable through the use of non-aqueous electrolytes with larger electrochemical windows (~5V for that of acetonitrile) and organic or metallo-organic redox compounds with potentially higher solubilities [3]. Recently, complexes such as metal acetylacetonates have demonstrated this principle by producing open circuit voltages over 2V and theoretical energy densities comparable to aqueous systems [4]. Therefore, such non-aqueous systems are very promising candidates, however they currently pose significant challenges to overcome; namely low solubilities and the lack of suitable membrane materials.
The work by our group investigates the electrochemistry of new materials, such as the complexes of cobalt(II) with pyridine-azole type ligands [5], and attempts to improve their properties, such as solubility, for their use in non-aqueous RFBs. Such complexes have desirable electrochemical properties for RFB applications due to; variable oxidation states which allows the construction of a single metal system, non-innocent ligand behavior which increases the cell voltage and modifiable ligand structures which allow tunable properties such as an increased solubility.

References

[1] J. Noack, N. Roznyatovskaya, T. Herr, P. Fischer, Angew. Chemie Int. Ed. 54 (2015) 9776–9809.

[2] B. Dawoud, E. Amer, D. Gross, Int. J. Energy Res. 31 (2007) 135–147.

[3] Y. Huang, S. Gu, Y. Yan, S.F.Y. Li, Curr. Opin. Chem. Eng. 8 (2015) 105–113.

[4] J.A. Suttil, J.F. Kucharyson, I.L. Escalante-Garcia, P.J. Cabrera, B.R. James, R.F. Savinell, et al., J. Mater. Chem. A. 3 (2015) 7929–7938.

[5] N.M. Shavaleev, F. Kessler, M. Grätzel, M.K. Nazeeruddin, Inorganica Chim. Acta. 407 (2013) 261–268.

P05

In-situ Measurements of Future Battery Technologies

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There are many incentives to move beyond the lithium-ion battery widely used today, in particular increased energy density. There are also secondary concerns related to the materials employed, spanning from safety and environment to economy and supply/demand. Despite wide scientific efforts, the implementation of these "next generation batteries" has remained stagnant, owing to key unsolved problems: short cycle life, low energy efficiency and low power density [1].

Here the scenario for the zinc-air battery is presented, where sources for instabilities are outlined (Fig. 1), and approaches to observe them in-situ in is discussed.

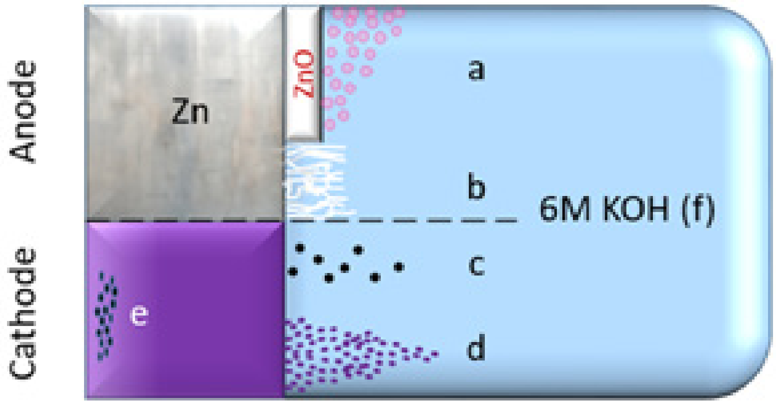

Figure 1. Common side reactions in Zn-air batteries [2]:
a) Hydrogen evolution reaction (HER), and formation of a passivating surface film
b) Zn dendrimerisation upon recharge.
c) Detachment of electrocatalyst support by peroxide attack.
d) Cathode dissolution from electrocatalyst disproportiation.
e) Clogging of the O2-selective air diffusion membrane from K2CO3 precipitate.
f) O2-membrane functionality reduction by caustic electrolyte attack.

References

[1] J. Wang, Y. Li, X. Sun, Challenges and opportunities of nanostructured materials for aprotic rechargeable lithium-air batteries, Nano Energy. 2 (2013) 443–467. doi:10.1016/j.nanoen.2012.11.014.

[2] Z. Ma, P. Pei, K. Wang, X. Wang, H. Xu, Y. Liu, et al., Degradation characteristics of air cathode in zinc air fuel cells, J. Power Sources. 274 (2015) 56–64. doi:10.1016/j.jpowsour.2014.10.030.

P06

Fundamental Analysis on the Effect of Nitrogen Doping in SnO_2 Anode for Li-ion Battery

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Tin (IV) oxide has been extensively studied as an anode material due to its low operating voltage as well as high specific and volumetric capacity.[1] One key problem in employing conversion-alloying based materials is the rapid capacity fading, which is usually caused by pulverization and agglomeration during cycling. Nanostructuring and elemental doping are alternatives that improve the performance of the material by directly altering both the physical and electronic structure of the crystal. Doping of nitrogen in SnO_2 (N-doped SnO_2) has not been extensively studied, while most of the works focus on simulations. For example, Sun et al showed that N is energetically favorable for substituting O under O/Sn-rich conditions and would lead to reduction in band gap.[2] Herein, we synthesized N-doped SnO_2 via laser pyrolysis and employed it as an anode material in LIBs. Key advantages of the as-synthesized powders that led to the excellent performance can be attributed to i) small particles with high surface area that leads to enhanced ion diffusion while mitigating pulverization/agglomeration during cycling; ii) direct N-doping into the structure of SnO_2 is made possible using this method, which led to enhanced conductivity and rate performance. Under precise control of nitrogen, the sample containing 3% N was capable of achieving an unprecedented capacity of 522 mAh g^{-1} per gram of active material under high current conditions 10 A g^{-1} at room temperature and a reversible capacity of 1192 mAh g^{-1} after 500 cycles at 1.4 A g^{-1}. Attempts to increase N concentration resulted in reduction of Sn^{4+} into Sn^0, which is inversely accompanied by more sluggish kinetic. XAS was utilized to monitor the position and the function of N dopant as well as to investigate the local chemical state of Sn during cycling. The exceptional conductivity and cyclability could be attributed to the presence of an unreactive Sn-N bonding in the structure during charge/discharge.[3]

References

[1] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa and T. Miyasaka, Science, 1997, 276, 1395-1397.

[2] X. Sun, R. Long, X. Cheng, X. Zhao, Y. Dai and B. Huang, The Journal of Physical Chemistry C, 2008, 112, 9861-9864.

[3] L.P. Wang, Y.Leconte, Z. X. Feng, C. Wei, Y. Zhao, Q. Ma, W. Q. Xu, S. Bourrioux, P. Azais, M. Srinivasan and Z. J. Xu. Submitted

P07

Stability assessment of transition metal sulfide based counter electrode for dye-sensitized solar cells

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In order to reduce the fabrication cost and minimize the corrosion effect by the iodine based electrolytes, research on the Pt-free alternative counter electrode for dye-sensitized solar cells (DSSCs) have bloomed in last decades. Among materials explored so far, transition metal sulfides (MS_x) have received much attention as they are low-cost and can be easily be prepared under atmosphere conditions, which is beneficial for mass production. Nevertheless, a systematic assessment on the long-term stability of the DSSCs with MS_x as counter electrode is relatively lacking.
Herein, the assessment on the long-term stability of DSSCs with cobalt sulfide (CoS) and nickel sulfide (NiS) as counter electrodes under both 1 sun illumination (100 mW cm^{-2}) and indoor light illumination (T5) is reported. CoS and NiS thin film (~300 nm) were directly deposited onto FTO substrate using a simple and scalable chemical bath deposition under mild conditions (90 °C). The DSSC was fabricated by placing the counter electrode over the N719 dyed mesoporous anatase TiO2 (~ 12 μm) photoanode and sealing the cell with 60 μm of surlyn hot-melt polymer film. An acetonitrile solution containing 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.5 M tert-butylpyridine, 0.03 M I_2, and 0.1 M guanidine thiocyanate was the electrolyte, and it was loaded into the cell via capillary force. Under 1 sun illumination, power conversion efficiencies (η) of DSSCs with NiS and CoS as counter electrodes are 6.99 ± 0.12% and 6.62 ± 0.23%, respectively, which are comparable to that with Pt as counter electrode (6.82 ± 0.21%). In addition, after the DSSCs were operated at elevated temperature (50 °C) and light soaking conditions (100 mW cm^{-2}) for 480 h, DSSCs with CoS and NiS as counter electrodes remained ~80% of their initial η, whereas the DSSC with Pt as counter electrode only remained ~70% of its initial one. Further studies on the effects of thermal aging on cell performance and the charge transfer kinetics governing DSSCs operation at MS_x|electrolyte and MS_x|FTO interfaces using electrochemical impedance spectroscopy, cyclic voltammetry, and linear sweep voltammetry are underway.

P08

Valence Change Ability and Geometrical Occupation of Substitution Cations Determine the Pseudocapacitance of Spinel Ferrite XFe_2O_4 (X = Mn, Co, Ni, Fe)

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In recent years, spinel ferrites have attracted much attention as a merging material for oxygen reduction reaction (ORR) [1], advanced battery electrodes [2] and supercapacitors [3]. However, the energy storage/conversion mechanism on spinels remains unclear. This poster reports a mechanistic study on the pseudocapacitive behavior of spinel XFe_2O_4 ferrites (X = Mn, Fe, Co, Ni). Since the charge storage occurs at the surface region, ferrite nanoparticles with diameter less than 10 nm were chosen as the model materials to ensure the dominant contribution of the surface region to X-ray absorption spectroscopy. $MnFe_2O_4$ showed nearly an order-of-magnitude higher capacitance than the other ferrites. In situ X-ray absorption spectroscopy studies demonstrated that only Mn cation is able to change its valence remarkably under applied potentials. Furthermore, it was found that the geometrical site occupation of Mn cations is influential on the capacitance of $MnFe_2O_4$. Having more Mn cations in octahedral sites will lead to an increase of capacitance. The results indicate that both the ability of cations to change their valence state and the occupation of such cations are influential in determining the pseudocapacitive behavior of spinel ferrites.

References

[1] Wei, C.; Feng. Z.; Scherer, G.G.; Barber, J.; Shao-Horn, Y.; Xu, Z.J. Cations in octahedral sites: a descriptor for oxygen electrocatalysis on transition metal spinels. 2016, Submitted.

[2] Feng, Z.; Chen, X.; Qiao, L.; Lipson, A. L.; Fister, T. T.; Zeng, L.; Kim, C.; Yi, T.; Sa, N.; Proffit, D. L.; Burrell, A. K.; Cabana, J.; Ingram, B. J.; Biegalski, M. D.; Bedzyk, M. J.; Fenter, P. Phase-controlled electrochemical activity of epitaxial Mg-spinel thin films. ACS Appl. Mater. Interfaces 2015, 7, 28438-28443.

[3] Wei, C.; Feng, Z.; Baisariyev, M.; Yu, L.; Zeng, L.; Wu, T.; Zhao, H.; Huang, Y.; Bedzyk, M. J.; Sritharan, T.; Xu, Z. J. Valence change ability and geometrical occupation of substitution cations determine the pseudocapacitance of spinel ferrite XFe2O4 (X = Mn, Co, Ni, Fe). Chem. Mater. 2016, in Press.

P09

Comparative study on the morphology of Cu deposited-gas diffusion electrode for electrochemical CO2 reduction

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Of late, electrochemical reduction of CO_2 to value-added chemicals (e.g. formate, ethanol, ethylene etc.) is touted as one of the most promising approaches to solve the global climatic problem and energy crisis [1]. Among a variety of metals, Cu has been intensively studied as a catalyst material due to its unique intrinsic property converting CO_2 into various hydrocarbons [2-4]. Herein, we study the morphological effect of Cu electrode on the catalytic activity, selectivity and stability. Cu is electrochemically deposited on the gas diffusion layer (GDL) for enhancing structural durability and reaction interface. According to the experimental conditions such as pH and applied cathodic potential during the electrochemical deposition, particle size, crystallinity and a degree of dispersion are controllable [5]. The importance of surface morphology on the metal substrate in electrochemical CO_2 reduction has been often considered [6,7] but there is much more to be investigated for carbon-based substrate such as GDL. We hope that this study will be applicable to next technologies for modularization and scale-up of practical-electrochemical gaseous CO_2 reduction system.

References

[1] Lee J, Kwon Y, Machunda RL, Lee HJ. Chem. Asian J. 4 (2009) 1516-1523.
[2] Hori Y, Kikuchi K, Murata A. Chem. Lett. (1986) 897-899.
[3] Kim D, Lee S, Ocon JD, Jeong B, Lee JK, Lee J. Phys. Chem. Chem. Phys. 17 (2015) 824-830.
[4] Lee S, Kim D, Lee J. Angew. Chem. Int. Ed. 54 (2015) 1-6.
[5] Grujicic D, Pesic B. Electrochim. Acta 47 (2002) 2901-2912.
[6] Tang W, Peterson AA, Varela AS, Jovanov ZP, Bech L, Durand WJ, Dahl S, Norskov JK, Chorkendorff I. Phys. Chem. Chem. Phys. 14 (2012) 76-81.
[7] Lu Q, Rosen J, Jiao F. ChemCatChem 7 (2015) 38-47.

P10

The influence of Rh in Pt-Sn/C nanocatalyst for ethanol oxidation: Physical and electrochemical characterization

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Carbon supported bimetallic Pt-Sn and trimetallic Pt-Sn-Rh nanocatalysts were synthesized by Bönnemann's colloidal precursor co-reduction method [1]. Electrochemical characterization of the catalysts regarding their onset potentials, activities and current densities towards ethanol oxidation were determined by linear sweep voltammetry. The relationship between the catalyst structure and catalyst activity of was evaluated by various microscopic and spectroscopic characterization techniques such as X-ray diffraction (XRD), High resolution transmission electron microscopy (HR-TEM), Energy dispersive X-ray analysis (EDX), and in-situ Fourier transform infrared spectroscopy (FTIR) [1, 2]. It was found that the catalytic property of Pt-Sn/C for the ethanol oxidation is favorably altered in the presence of Rh. To understand the benefits of Rh in the structure of Pt-Sn/C, HR-TEM and EDX spectroscopy techniques was very helpful since the particles with different phases such as SnO_2 species can be clearly observed from high resolution images. The analysis result showed that SnO_2 and Pt-Rh exist as separate state in the Pt-Sn-Rh/C catalyst (Fig. 1). The change in the Pt lattice due to the addition of Rh and to interaction between Pt and Rh, both of which favors C–C bond cleavage in the ethanol molecule, while the CO-intermediates formed during breaking of C–C bond were removed by the SnO_2 surface species.

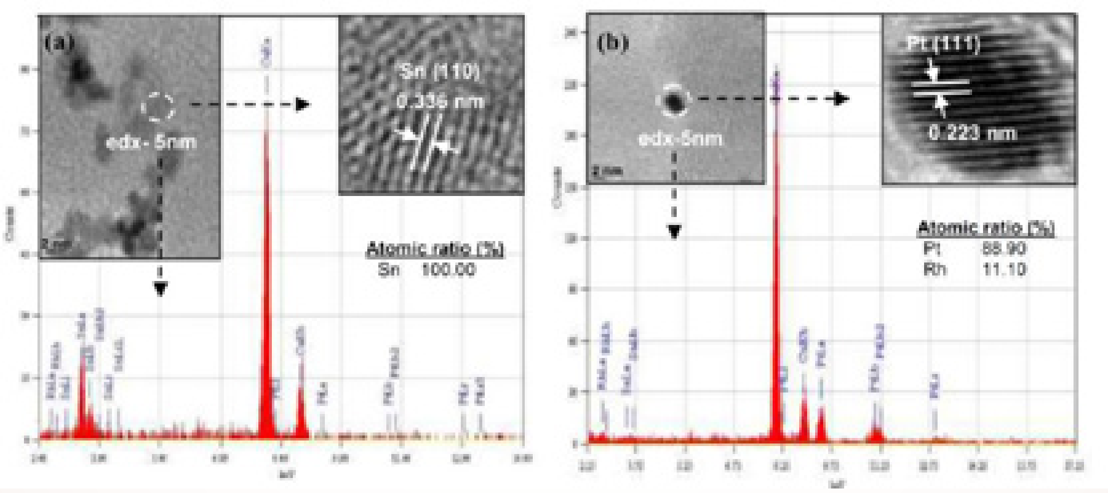

Figure 1. HRTEM images of Pt-Sn-Rh/C catalyst together with EDX analysis of the selected areas, showing the particle has the SnO2 structure (a) and Pt structure (b using a 5 nm electron beam.

References

[1] Beyhan S, Coutanceau C, Léger JM, Napporn TW, Kadırgan F. Int. J. Hydrogen Energy **38** (2013) 6830.
[2] Beyhan S, Léger JM, Kadırgan F. Appl. Catal B. Environ. 144 (2014) 66.

P11

Decoration of cobalt with a fiber structure with gold nanoparticles for hydrazine oxidation

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This work is focused on the study of electrocatalytic activity of cobalt with a fiber structure deposited on the copper surface and decorated with gold nanoparticles towards the oxidation of hydrazine. Cobalt coatings having a fiber structure and with the thickness of ~3 μm were deposited on the copper surface. Au crystallites were deposited on the Co/Cu surface via the galvanic displacement technique. The Co/Cu electrodes were immersed into the 1 mM $HAuCl_4$ + 0.1 M HCl solution at 25 ^{o}C for 0.5, 1 and 5 min [1]. The morphology, structure and composition of the prepared catalysts were examined by means of Field Emission Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy, X-ray diffraction and Inductively Coupled Plasma Optical Emission Spectroscopy. Electrocatalytic activity of the prepared Au(Co)/Cu catalysts was investigated by means of cyclic voltammetry and chrono-techniques.

The Au(Co)/Cu catalysts having Au loadings of 11, 22 and 84 μg cm^{-2} were prepared after the immersion of the Co/Cu electrodes into the gold-containing solution for 0.5, 1 and 5 min, respectively. It was found that the cobalt with a fiber structure and decorated with the Au nanoparticles in size of ca. 10-50 nm show enhanced electrocatalytic activity towards the oxidation of hydrazine in an alkaline medium as compared to that of bare Au and Co.

References

[1] Tamašauskaitė-Tamašiūnaitė L, Jagminienė A, Balčiūnaitė A, Zabielaitė A, Vaičiūnienė J, Selskis A, Juškėnas R, Norkus E. Int. J. Hydrogen Energy 38 (2013) 14232-14241.

P12

Electrochemical Oxidation of C3 Saturated Alcohols on Co_3O_4 in Alkaline Solution

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Based on our previous work, C1 and C2 alcohol oxidation on Co_3O_4 has been inveistigated in alkaline solution.[1-2] Considering the to the complexity increase in molecular structure and types of C3 saturated alcohols compared with C1 and C2 alcohols, it is more interesting and challenging to investigate the C3 saturated oxidation in alkaline solution. This work presents a systematic study on electrochemical oxidation of C3 saturated alcohols (propanetriol, 1,2-propanediol, 1,3-propanediol, 1-propanol, and 2-propanol) on Co_3O_4 in alkaline. Co_3O_4 electrodes were prepared by electrodeposition of $Co(OH)_2$ on graphite paper, followed by annealing in air. The electrocatalytic activities of Co3O4/graphite paper electrode (Co_3O_4/GPE) toward C3 saturated alcohol electro-oxidation were investigated by using cyclic voltammetry, multi-step chronoamperometry, and electrochemical impedance spectroscopy techniques in 1.0 M KOH solution. It was found that the performance of Co_3O_4 for C3 saturated oxidation exhibited a trend: propanetriol (GLY), 1,2-propanediol (1,2-P), 1,3-propanediol (1,3-P), 1-propanol (1-P), and 2-propanol (2-P). The influence of KOH concentration on C3 saturated alcohol oxidation was reflected by cyclic voltammetry method. The KOH concentration varied from 0.5 to 5.0 M. Higher concentration of KOH can facilate the oxidation reaction, especially for those alcohols bearing secondary hydroxyl group like GLY and 1,2-P. The products from C3 saturated alcohol oxidation were analyzed by nuclear magnetic resonance, which indicated that when there existed the adjacent hydroxyl groups, the coresponding C-C bond can be readily broken up. X-ray absorption near-edge structure (XANES) spectroscope study suggested that the supply rate of high valence of cobalt was faster than that of cobalt reduction to low valence state by alcohol.

References

[1] Sun S, Xu Z. Electrochimica Acta 165 (2015) 56-66.
[2] Sun S, Zhou Y, Hu B, Zhang Q, Xu Z. J. Electrochem. Soc. 163 (2) (2016) H99-H104.

P13

Potential-Dependent Behavior of Hexadecane Droplets on Au Electrode Surfaces

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Liquid alkanes show a potential-dependent dynamic behavior at electrified interfaces in an aqueous solution. A hexadecane (HD) droplet (75 μL) exhibits macroscopic morphological change on a Hg electrode [1]. A HD monolayer undergoes order-disorder transition on a Au(111) electrode surface in a EC-STM image [2].
We focus on the potential dependent morphologies of HD adlayers and droplets (1 μL) on a Au(111) electrode surface to reveal the factors determining the wettability of alkane at a mesoscopic level. Especially, the effect of coexistent electrolyte ions and a surfactant (sodium dodecyl sulfate: SDS) on the dynamics were studied. Also, the dependence on an electrode surface facet structure was examined.
HD adlayers and droplets were deposited on a Au(111) electrode surface in various electrolyte solutions (0.5 M $KClO_4$, KBr, KF, H_2SO_4). Measurements of voltammograms and in situ fluorescence microscopic images were carried out by the use of a Ag/AgCl/sat'd KCl reference electrode in an Ar gas atmosphere at room temperature. The fluorescent microscopic measurements unveiled the movements of small HD droplets in the surface-normal direction.
In $KClO_4$ solution, the contact angle (θ) of HD droplet (1 μL) on a Au(111) electrode surface showed hysteresis between −0.6 ~ −0.2 V. At the potentials of $E > 0.0$ V, the value of θ was constant. In KBr solution, the change of θ was governed by potential dependent Br^- adsorption/desorption around the droplet periphery on the Au(111) electrode surface. In SDS solution, a sudden change of θ corresponded to the phase change of a DS^- adlayer from hemi-micelle to interdigitated bilayer on the electrode surface. In H_2SO_4 solution, a stepwise change of θ was found at $E = 0.45$ V. At this potential, SO_4^{2-} adsorbs on the Au(111) electrode surface. A HD droplet on a Au(110) electrode surface, in sharp contrast to Au(111), did not show any θ change in various electrolyte solutions.
Taken together, the adsorption of electrolyte anions is a dominant factor of the potential dependent behavior of HD droplets. The change in the interface tension at the Au(111)/solution interface is determined by anion adsorption or by the phase change of the underlayer. At a Au(110) surface, HD molecules attract the Au surface atoms more strongly than electrolyte ions and even water molecules do. As a result, the θ change does not occur as a function of E at a Au(110) electrode.

References

[1] Inošević N, Žutić V, Langmuir 14 (1998) 231-234.
[2] He Y, Ye T, Borguet E, J. Phys. Chem. B 106 (2002) 11264-11271.

P14

Electroless deposition of platinum studied by EQCM

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In recent years electroless metal deposition is widely used for metallization of various dielectrics, fabrication of mirrors, galvanoplastic, formation of catalysts used in fuel cells, fabrication of microcircuit, optoelectronic, etc. An efficiently strong reducing agent is required for autocatalytic metal deposition. The use of traditional reducing agents (formaldehyde, borohydride, hypophosphite, etc.) is limited due to simultaneously occurred the parasitic reactions with the oxidation of reducing agent: the deposited coatings have a structure with large defects. In the present study we have been used a new type of the reducing agent – Co(II)/Co(III) redox system for reduction of Pt(IV) ions, which allows to solve this problem.
Electrochemical quartz crystal microgravimetry (EQCM) was used for the investigation of kinetics of electroless deposition of Pt layer on the copper surface under various conditions. It was found that the deaeration of the electroless Pt plating solution with argon results in higher deposition rate of Pt. Electroless Pt deposition rate is ca. 0.3 μg cm^{-2} min^{-1} when using Ar-deaerated plating solution. In the case of non-deaerated plating solution, Pt deposition rate is significantly lower, e.g. 0.02 μg cm^{-2} min^{-1}. The morphology and structure of the surface of deposited Pt layers were examined by means of Field Emission Scanning Electron Microscopy.

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P15

Exploring the impact of semicore level electronic relaxation on polaron dynamics

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Many novel materials used in clean energy applications such as lithium iron phosphate (Li_xFePO_4), hematite, and certain perovskites are known to exhibit polaronic behavior. Being transition metal oxides, the strongly correlated interaction of the d shell electrons opens a gap and localizes conduction electrons into polaronic states, leading to the hopping conduction observed in these materials. To model electronic conductivities from a theoretical point of view, it is therefore necessary to calculate activation energies of such polarons. We study the effects of the electronic relaxation of semicore levels on polaron activation energies and dynamics. Within the framework of adiabatic ab initio theory, we utilize both static transition state theory and molecular dynamics methods for an in-depth study of polaronic hopping in our model system of Li_xFePO_4. Our results show that electronic relaxation of semicore states is significant in Li_xFePO_4, resulting in a lower activation barrier and kinetics that are one to two orders faster compared with calculations that do not incorporate semi-core states. In general, the results suggest that the relaxation of states far below the Fermi energy could dramatically impact upon ab initio polaronic barrier estimates for many transition metal oxides and phosphates.

P16

Smart Nanostructured Interface based on Immobilized Redox Active Ionic Liquids

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Surface chemistry plays a relevant role in the physical and chemical properties of electrode materials for various applications such environmental protection, energy storage, biomaterials, chemical sensors, biosensors, catalysis, and photocatalysis. For electrochemical applications, ionic liquids are intrinsic solvents and electrolytes. They are been reviewed extensively for their wide range of applications. However, the unendurable viscosity of ionic liquids and from issues associated with cost and toxicity limit their further applications to the industrial scale to some extent. The immobilization of ionic liquid on solid supports can solve these problems and satisfy the requirements from the chemical industry. The ongoing challenge is to link fundamental studies on ionic liquids to their improved performance in technological applications. Because of the great interest in the potential of ionic liquids as alternative materials in diverse electrochemical applications, studies on the properties of molecular assemblies of ionic liquids have become important.

Recently, we have developed a new family of ionic liquids that exhibit well-defined redox properties. Herein, we will report the surface modification of carbon materials by means of electrografting [1-5]. Electrochemical processes based on oxidative or reductive grafting have been used for the attachment of organic molecules, such as redox active ionic liquids, onto various electrode surfaces providing new and special properties to the interfaces. The immobilization of redox active poly(ionic liquid) by surface-initiated atom transfer radical polymerization (SI-ATRP) process onto electrode surfaces has been investigated. The surface and electrochemical properties of these modified surfaces were investigated by combining different techniques (XPS, AFM, ellipsometry, and contact angle). The nanostructured redox active poly(ionic liquid) exhibits high heterogeneous electron transfer rate about 150 s^{-1} [6]. We will show the use of redox active poly(ionic liquid) polymer brush as electrochemically reversible tunable surface wettability system and as electrochemical sensors (pH sensors, and detection of biomolecules).

References

[1] Gomez-Mingot M, Bui-Thi-Thuyet V, Trippé-Allard G, Ghilane J, Randriamahazaka H, ChemElectroChem. 1 (2014) 1467-1470.

[2] Bui-Thi-Thuyet V, Trippé-Allard G, Ghilane J, Randriamahazaka H, J. Electroanal. Chem. 713 (2014) 28-31.

[3] Bouden S, Trippé-Allard G, Ghilane J, Randriamahazaka H, Electrochem. Commun. 58 (2015) 65-68.

[4] Randriamahazaka H, Ghilane J, Electroanalysis, 28 (2016) 13-26.

[5] Bouden S, Gomez-Mingot M, Randriamahazaka H, Ghilane J, Anal. Chem. 88 (2016) 2017-1021.

[6] Bui-Thi-Thuyet V, Trippé-Allard G, Ghilane J, Randriamahazaka H, ACS Appl. Mater. Interfaces, in revision.

P17

Electronic Structure of the CO/Pt(111) Electrochemical Interface Probed by Potential-Dependent Double Resonance Sum Frequency Generation Spectroscopy

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Absorbed CO/Pt interface has been studied extensively as a model system in ultra-high vacuum (UHV), gas phase and electrochemical conditions since adsorbed CO plays an important role in many catalytic reactions, such as water-gas shift reaction and methanol fuel cell reaction. Detailed understanding of the in situ information at CO/Pt interfaces, including geometric, molecular and electronic structures, is essential to understand the role of CO in the reactions and improve the efficiency of the reactions. A large number of fundamental studies on interfacial geometric, molecular and electronic structures of CO/Pt in UHV and geometric and molecular structures of CO/Pt in electrochemical environment have been carried out in the last thirty years. However, only a few works are available on electronic structure of CO/Pt in electrochemical environment [1] because the techniques, which usually use electron as a probe to determine the electronic structure in UHV, cannot be applicable to electrochemical interfaces due to the presence of liquid. Double resonance sum frequency generation (DR-SFG) spectroscopy, which utilizes resonant enhancement of SFG signal with both frequency-tunable incident IR and visible lights, has been proved to be able to elucidate the electronic structure of CO/Pt interface in UHV [2], and it should be applicable to electrochemical interfaces since it is a photon-in photon-out technique.

In the present study, potential-dependent DR-SFG technique was used to determine the electronic structure of CO/Pt(111) interface in a CO-free 0.5 M H2SO4 solution by using visible light of eight different energies [3]. The intensity of the SFG peak due to C-O stretching vibration anomalously increased prior to anodic CO oxidation and the potential of the anomalous SFG intensity peak linearly depended on the incident visible energy with a slope of 1V/eV, showing the origin of the increase of the SFG intensity is not due to the potential-dependent geometric structure change of adsorbed CO as suggested before [4] but due to a surface electronic resonance, in which the energy of visible and/or SF light becomes equal to the energy of interfacial electronic transition from the Fermi level of Pt(111), which is tuned by the electrode potential, to the 5□a antibonding state of adsorbed CO. The effect of substrate on the electronic structure of CO/Pt was also investigated by applying this technique to various electrode surfaces such as polycrystalline Pt electrode and Pt thin layers of different thickness deposited on Au substrates.

References

[1] P Simon, Y Gogotsi, B Dunn, Science, 34 (2014), 1210-1211.

[2] S Chu, A Majumdar, Nature 488 (2012) 294-295.

[3] P H Yang, Y Ding, Z Y Lin, Z W Chen ,Y Z Li, P F Qiang, M. Ebrahimi, C P Wong , Z L Wang, NanoLett.14 (2014) 731-736.

P18 Electrochemical deposition of Yttrium for CRT waste recovery

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Yttrium is a silvery metallic transition metal chemically similar to lanthanides. It is a substantial element for construction of CRT screens and its content in CRT waste is significant. Electrochemical deposition was tested as a method for Yttrium recovery from CRT waste.

Cathodic electrochemical deposition of Yttrium films was carried out at ambient temperature in an open glass two compartment three electrode cell (ITO glass as a working electrode and Pt as a counter electrode vs. calomel reference electrode). Experimental conditions to obtain homogeneous deposits (films) were determined. An ICP standard solution of Yttrium was used as a working electrolyte. The structural and morphological characteristics of the products were determined by XPS scanning electron microscopy (SEM), EDX and Raman spectroscopy. Electrochemical deposition was carried out in a cyclic voltammetry mode which enabled deposition of uniform and clearly visible film. The XPS results have shown that with different binding energies, at least two oxidation states of Yttrium exists in the deposited film and this was also confirmed by Raman spectroscopy. The optimal range of working potential was shown to be ± 1.5 mV.

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Financal support of Technology Agency of the Czech Republic (Project no. TA04020130) is gratefully acknowledged.

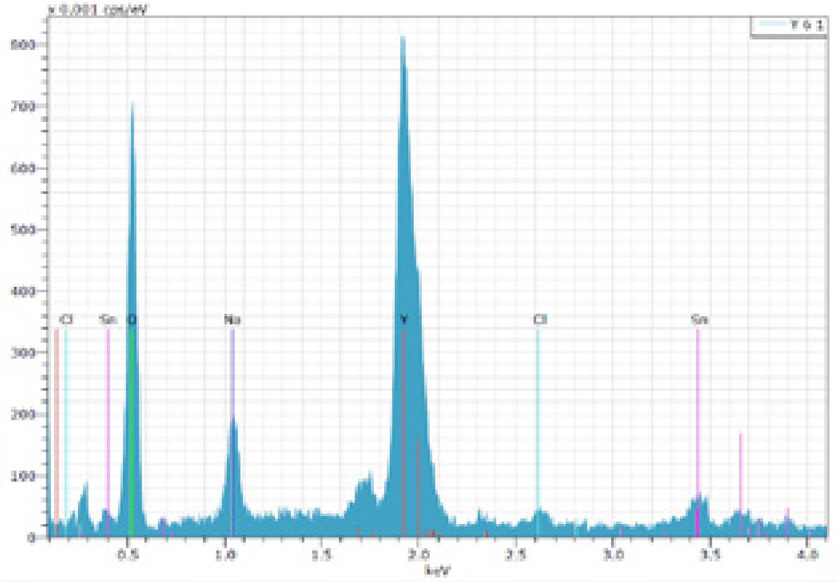

Figure 1. EDX analysis of Yttrium deposited film on ITO glass

P19

On the composition effects on the catalytic activity of iron oxide toward electrochemical water oxidation

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In this work, we report on the iron oxide based materials for the electrocatalytic water oxidation. n-type and p-type iron oxide thin film was prepared by spin-coating and follow-up thermal treatment, and the type of conductivity of iron oxide was controlled by adding other elements during the film preparation. As shown in Figure 1a, the p-type iron oxide showed superior electrocatalytic activity than n-type ones; the overpotential (η) required to achieve current density of 1 mA cm^{-2} and 10 mA cm^{-2} for p-types are about 430 mV and 530 mV, respectively, which is much lower than those for n-type iron oxide (η@ 1 mA cm^{-2} =~530 mV, η@ 10 mA cm^{-2}= ~ 770 mV). In addition, at applied current density of 1 mA cm^{-2} for 30 min, the change in η is insignificant (< 5 mV, see Figure 1b). Further studies on mechanism behind are underway.

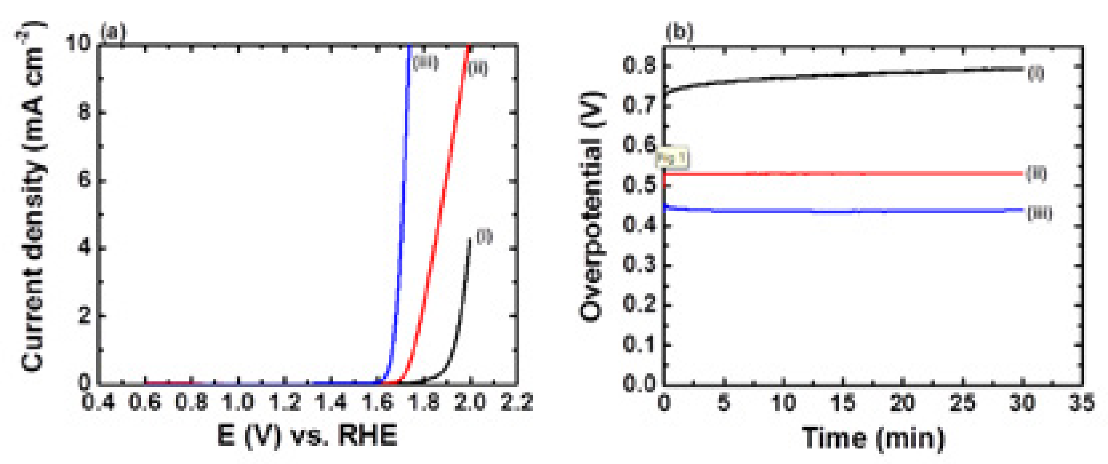

Figure 1. (a) Linear sweep voltammetry, recorded at 10 mV s^{-1}, and (b) chronopotentiogram, at an applied current density of 1 mA cm^{-2}, of (i) FTO substrate, (ii) n-type iron oxide coated FTO substrate, and (iii) p-type iron oxide coated FTO substrate in 0.1 M NaOH solution (pH 13.2). All the electrochemical characterizations were carried out in two-compartment (separated by a Nafion® 117 film) electrochemical cell without i-R compensation.

P20

A Facile Synthesis of Size-Controllable IrO$_2$ and RuO$_2$ Nanoparticles for the Oxygen Evolution Reaction

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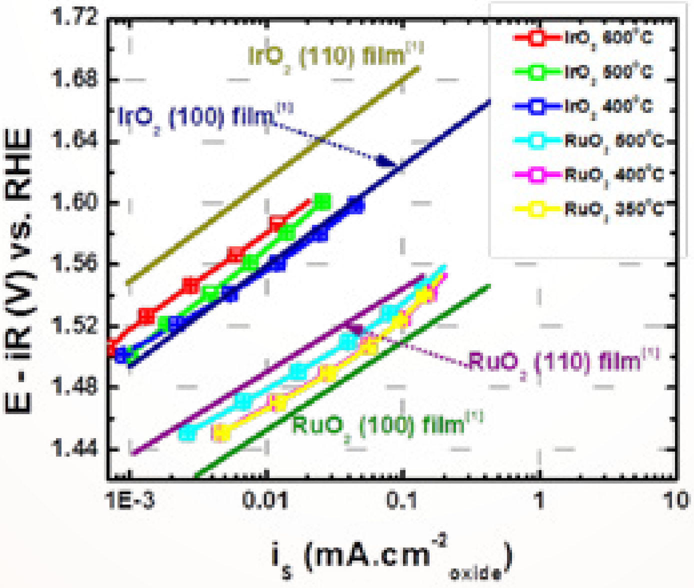
Sluggish kinetics of the oxygen evolution reaction (OER) is the main factor that restricts the efficiency of the water electrolysis process. Some effective catalysts, such as IrO$_2$ and RuO$_2$, have been developed to improve the kinetics of the OER and therefore the overall efficiency of the water electrolysis [1]. This report presents a facile wet-chemical method for synthesizing IrO$_2$ and RuO$_2$ nanoparticles (NPs) for the OER. The nanoparticles were synthesized by reducing metal chlorides in ethylene glycol in the presence of polyvinylpyrrolidone, followed by annealing in air at different temperatures to control the particle size. The activity of IrO$_2$ and RuO$_2$ NPs was investigated by cyclic voltammetry (CV) in alkaline (0.1 M KOH) electrolyte. As-synthesized IrO$_2$ and RuO$_2$ NPs showed high catalytic activity for the OER. The IrO$_2$ NPs exhibited a specific activity of up to 3.5 (± 1.6) $\mu A/cm^2_{oxide}$ at 1.53 V (vs. RHE), and the RuO$_2$ NPs achieved a value of 124.2 (± 8) $\mu A/cm^2_{oxide}$. For mass activity, RuO$_2$ NPs showed a value up to 102.6 (±10.5) A/g_{oxide} at 1.53 V (vs. RHE), which is the highest reported to date. Moreover, a correlation between specific activity and crystal orientation of IrO$_2$ and RuO$_2$ NPs was also observed. The crystal orientation is considered as one of the main governing factors that control the OER activity.



References

[1] Stoerzinger, K. A.; Qiao, L.; Biegalski, M. D.; Shao-Horn, Y. Orientation-Dependent Oxygen Evolution Activities of Rutile IrO2 and RuO2. J. Phys. Chem. Lett., 2014, 5, 1636−1641.

P21

Synthesis of saw-toothed palladium-platinum nanocubes and their electrocatalysis in oxygen reduction reaction

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A simple method for the efficient synthesis of saw-toothed Pd-Pt nanocubes by using Pd nanocubes as reactants has been developed. Through the introduction of PtCl62- ions, the Pd nanocubes undergo sculpturing and displacement reaction to form saw-toothed Pd nanocubes with Pt-rich surface, which are Pd0.945Pt0.055 and Pd0.972Pt0.028 nanocubes precisely synthesized by molar ratio of 1/10 and 1/18 for Pt to Pd, respectively. Furthermore, these nanocubes are tested their feasibility for catalyzing alkaline oxygen reduction reaction (ORR). On the basis of the same loading mass of catalyst, the results of rotating ring-disk electrode measurements indicate that the 28.2 nm Pd0.945Pt0.055 nanocubes and 27.6 nm Pd0.972Pt0.028 nanocubes display kinetic current of 0.3673 mA and 0.3525 mA, respectively. These values are greater than the 0.2099 mA observed for 7.4 nm Pt nanoparticles and 0.215 mA observed for 27 nm Pd nanocubes. Additionally, a fair comparison supported by transmission electron microscopy and electrochemical data shows that the shapes of the saw-toothed nanocubes and their alloy structures are nearly unchanged by the ORR and that these alloy catalysts show stabilities superior to Pt nanoparticles.

P22

Development of electrocatalysts for ORR through the encapsulation of Pt into carbon nanochannels

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Oxygen reduction reaction (ORR) is one of the most important reactions for energy devices since reducing its overvoltage leads to improvement of energy efficiency. Similarly, the overvoltage at the cathode is a serious issue in the case of polymer electrolyte fuel cells (PEFCs). One of the solutions is increasing Pt catalyst active surface area by reducing the size of Pt nanoparticles. However, low durability of such small particles over the time is a problem for the practical use of PEFCs. Pt particles, whose size is a few nanometers, have a tendency to agglomerate, or dissolve and re-precipitate on carbon supports under the potential change, resulting in formation of larger particles. In this study, suppressing such Pt particle growth and then increasing durability of electrocatalysts are targeted by reducing the mobility of Pt particles on the carbon support. Based on the idea coming from the increased stability on the curved surface comparing to the flat surface, principally, Pt particles are introduced into nanochannels of mesoporous carbon (MC), whose diameter is ca. 10 nm. Electrocatalysts were synthesized from platinum(II) acetylacetonate as a precursor by supporting ca. 30 wt% Pt on our original MC, which was made from the self-organization formaldehyde/resorcinol and Pluronic F127[1].The resulting electrocatalyst was named as Pt/MC and used as a cathode catalyst. For the anode, a commercially available Pt/Ketjen black catalysts (TEC10E50E, TKK Corp.) was in use. Membrane electrode assemblies (MEAs) were prepared by spraying the dispersion containing catalyst and Nafion ionomer on both sides of Nafion membrane. For the comparison, Pt deposited on commercial available Vulcan XC72 carbon black (Pt/VC) was also made and used as a cathode catalyst.

Current-voltage (IV) characteristics of MEAs were measured in this study. Initial IV characteristic of Pt/MC-MEA resulted in same as that of Pt/VC-MEA. In order to evaluate durability of MEAs, accelerating degradation tests were performed using potential cycles between 0.6 and 1.0 V vs RHE, where dissolution and reprecipitation of Pt particles occur [2].When the change in the overvoltage was compared, the overvoltage resulted in lower for Pt/MC-MEA than Pt/VC-MEA after cycles. Therefore, encapsulation of Pt nanoparticles into carbon nanochannels successfully increased durability. Change in size of Pt particles before and after potential cycles was also evaluated by SEM/STEM images. As a result, the growth of Pt particles was found to be much suppressed within the nanochannels, which is most likely due to reduced Pt mobility inside the nanochannels.

References

[1] Hayashi A. et al., Electrochim. Acta, 53(21) 6117 (2008).
[2] Ohma A. et al., ECS Trans., 41, 755 (2011).

P23 Effects of Mn Valence and Occupation on Spinel Manganese Ferrite toward Oxygen Reduction/Evolution Reaction

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We design a set of experiments to inspect the underlying factors governing the intrinsic activity of spinel $MnFe_2O_4$ and hopefully to provide insights into the future design of efficient spinel catalysts. In manipulating the physiochemical properties of $MnFe_2O_4$ through a simple oxidative and reductive annealing procedure, the variation in Mn valency and distribution proceeds to an opposite way in air and Ar annealing atmosphere with rising temperature. Specifically, the oxidative annealing process in air oxidizes more Mn ions to its higher oxidation state and pushes more Mn cations to octahedral site with elevating temperature. While the reductive annealing in Ar atmosphere brings more Mn ions to its lower valence state (+2) and pushes more Mn cations to tetrahedral site. For the Fe cation, apart from being commute between the two geometric sites, it is quite stable in its valence state (~+2.7) during the whole annealing process. The Mn valence state dependence of oxygen reduction/oxygen evolution activity was obtained according to the characterizations. In air annealed $MnFe_2O_4$ specimens, the promoted specific activity with increasing amount of Mn^{3+} can be mainly attributed to the moderate eg filling as well established in perovskite octahedral B-site [1]. In this air annealing experimental line, a more inversed structure could be a slight promotor in the catalysis as the 400°C annealed MnFe2O4 shows an increased activity than the 300°C counterpart while the Mn valence in between exhibits no obvious gap. For the annealed $MnFe_2O_4$ in Ar atmosphere, a different direction should be adopted to perceive the catalytic activity trend as oxygen deficiency [2] is inevitably involved due to charge balance with more reduced Mn cations yield. Although the spinel experienced a more inversed structure to a near normal structure with inversion degree ranging from 55.6% to 18.5% in Ar annealing process, this inversion degree relegated to a secondary role and the introduction of oxygen vacancy could be a promoting factor in the catalytic activity in those Ar-annealed specimens.

References

[1] Jin Suntivich, Hubert A.Gasteiger, Naoaki Yabuuchi, Haruyuki Nakanishi, John B. Goodenough, Yang Shao-Horn, Nature Chemistry 3 (2011) 548.

[2] J.Tyler Mefford, Xi Rong, Artem M. Abakumov, William G. Hardin, Sheng Dai, Alexie M. Kolpak, Keith P. Johnston, Keith J. Stevenson, Nature Communication 7 (2016) 11053.

P24 Developing methods for in-situ TEM electrochemistry studies

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Conventional Transmission electron microscopy (TEM) can provide detailed information of complex nanostructures, including morphology, composition, and crystalline phases etc. Combining thin-film technology and microfabrication with TEM imaging have brought a new era to TEM, where the use of liquid cells enables studies of dynamic process with high spatial and temporal resolution. Remarkable research results have been demonstrated [1]; for instance intricate details of nucleation processes and crystal growth [2,3], electrochemical reactions of nanostructures in batteries [4], and commercial systems are also available now.

We here report on our ongoing development of a TEM liquid cells [5], with a new holder with liquid feedthroughs for flow and 5 electrical contacts to a liquid cell made of two clamped microchips with electron transparent SiNx windows as shown in the figure below. As with the commercial systems, the liquid environment in the system make it possible to conduct various electrochemistry experiments under TEM observation directly, e.g. processes related to battery chemistry, electrochemical deposition, etching and corrosion reactions. The 5 electrical contacts furthermore enables controlled localized heating of the liquid, and precise measurements of resistance and conductivity using 4 point measurements, or development of better reference electrodes that are currently a need for such liquid cells.

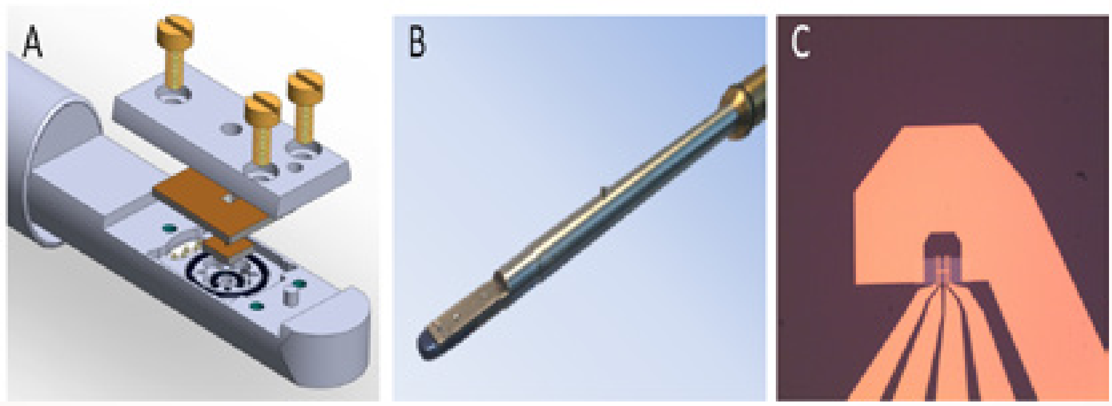

Figure 1. A) CAD drawing of TEM holder with liquid feedthrough for flow and 5 electrical contacts; B) Real picture of TEM holder; C). Optical image of a TEM chip electrodes for 4 point measurement and a large counter electrode.

References

[1] Ross FM, Science, 350 (2015) aaa9886.
[2] Nielsen MH, Aloni, S; De Y, James J. Science, 345 (2014) 1158-1162.
[3] Levlev AV, Jesse S, Cochell TJ, Unocic RR, Protopopescu VA, Kalinin SV, ACS Nano, 9 (2015) 11784–11791
[4] Gu, M; Parent, LR; Mehdi, BL, et al, Nano Lett. 13 (2013) 6106-6112
[5] Jensen E, Burrows, A, Mølhave, K, Microsc. Microanal. 20 (2014) 445–451.

P25

Electrocatalytic determination of formaldehyde on nickel modified electrodes

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The electrocatalytic conversion of CO_2 to produce useful hydrocarbon products, such as methanol, methane, and beyond is a deeply challenging process that invariably produces more than one product depending on the catalytic system. The complex multi-proton multi-electron step reactions yield an array of small organic products, the first 3 water-soluble products being formate, formaldehyde and methanol.

Despite increasing interest in this challenging field of research, it remains that a simple, selective and effective means of identifying and quantifying these small organic molecules, in a typically complex reaction medium, is a fundamental issue. Of particular note is formaldehyde. Developing methods to selectively, accurately and rapidly identify and quantify these products would therefore be of great advantage to CO_2 reduction research, not to mention a valuable analytical development in wastewater treatment and analysis.

A particularly problematic compound in electrocatalytic CO_2 reduction is formaldehyde. The compound is non-polar, unidentifiable by proton NMR in aqueous samples, non-volatile and too small for GC/MS methods. Standard analytical strategies to identify and quantify the molecule use complex derivitisation methods and UV/vis-HPLC. Electrochemical approaches would better suit quantification of the complex electrolyte expected of CO_2 reduction samples however. Such samples are unsuitable for chromatographic machinery, and sample preparation would potentially lose sample. A small body of research exists in the field of electrochemical formaldehyde determination, with approaches typically using platinum, palladium or gold electrocatalysts.

Here we report the use of a simple nickel modified glassy carbon electrode (Ni-GCE) used in alkaline solution to determine low concentrations of formaldehyde. The simply fabricated Ni-GCE demonstrated a clear and sensitive response to low concentrations of formaldehyde, typical of the electrocatalytic mechanism of NiOOH species in hydroxide. Detection limits of 10.9 µM (3.3 ppm) were obtained, which is comparable to electroanalytical responses obtained by precious metal modified electrodes [1-3]. This talk further discusses the selectivity and reproducibility of the Ni-GCE in the context of CO_2 reduction products.

References

[1] M. R. Baez-Gaxiola et al, Anal. Methods, 7, (2015), 538
[2] Y. Zhang et al, Electrochim Acta, 68, (2012), 172
[3[Z.-L. Zhou et al, Michrochim Acta, 164, (2009), 133

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Monte Carlo simulations of Li intercalation in $Li_xM_yMn_2O_4$: towards an increased understanding of entropy profiles

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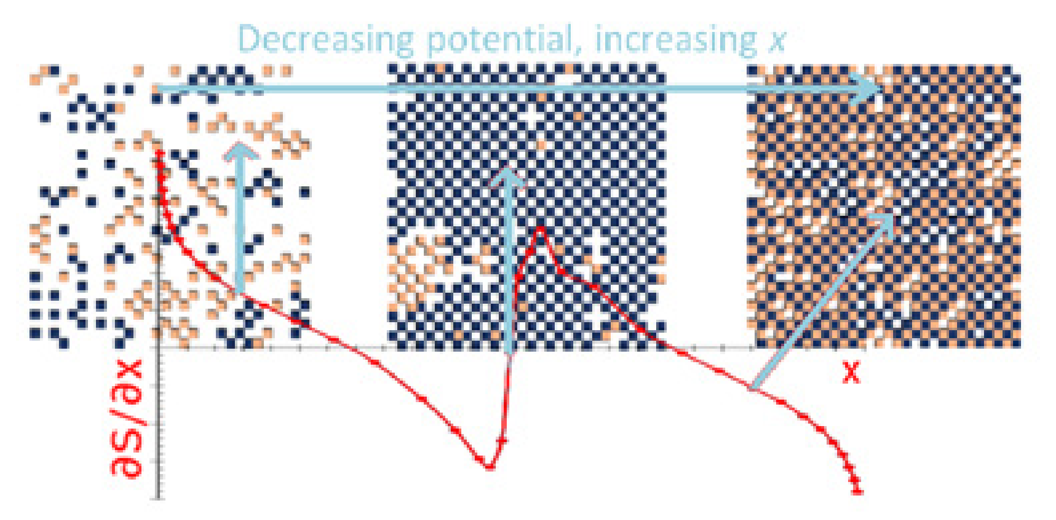
The long term stability of the cathode of Li-ion batteries is a major bottleneck in the performance. Entropy profiles are used to characterise the state of health of a battery [1]; these profiles are obtained by measuring the variation in the open circuit potential as a function of temperature [1-4]. There has been increased interest in understanding the physical origin of the changes observed in these profiles as the cathode becomes degraded through repeated charge-discharge cycles [2]. Here, we present a lattice gas Monte Carlo approach to understanding the profiles of $Li_xMn_2O_4$ that is based on an existing model [3]. In doing so, we observe an order-disorder transition in the Li sublattice, shown in Figure 1, replicating the results of Kim et al.. As an extension to this model we propose to introduce defects M (M = Co, Cr) that pin Li into the lattice to examine and quantify the effect of defect concentration on partial molar entropy changes, $(\partial/\partial x\ S_{(x)})_{p,x}$. Previously, this has only been performed qualitatively [5], or at best semi-quantitatively [6]. Our goal is to provide a descriptor to experimentalists to enable a more quantitative in situ comparison of the experimentally determined entropy profiles with the defect content of the cathode, potentially leading to an improved understanding of the degradation mechanisms.



References

[1] Y. Reynier, J. Graetz, T. Swan-Wood, P. Rez, R. Yazami, B. Fultz, Physical Review B 70 (2004) 174304.

[2] K. Maher, R. Yazami, Electrochimica Acta 101 (2013) 71-78.

[3] S.-W. Kim, S.-I. Pyun, Electrochimica Acta 46 (2001) 987-997.

[4] P. J. Osswald, M. del Rosario, J. Garche, A. Jossen, H. Hoster, Electrochimica Acta 177 (2015) 270-276.

[5] Y. Kobayashi, Y. Mita, S. Seki, Y. Ohno, H. Miyashiro, M. Nakayama, M. Wakihara, Journal of the Electrochemical Society, 155 (2008) A14-A19.

[6] T. Kashiwagi, M. Nakayama, K. Watanabe, M. Wakihara, Y. Kobayashi, H. Miyashiro, J. Phys. Chem. B, 110 (2006) 4998-5004.