

Nanoscale Physics of Electrochemical and Biological Media

748. WE-Heraeus-Seminar

**09 – 12 May 2021
Online via MeetAnyway**

**WILHELM UND ELSE
HERAEUS-STIFTUNG**



Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see <https://www.we-heraeus-stiftung.de>

Aims and scope of the 748. WE-Heraeus-Seminar:

Recent advances in theoretical, computational and experimental nanoscale physics shed increasingly light on the commonalities between electrochemical and biophysical media. In both cases, a material's functionality typically rests on the interplay of charged species in electrolytes, charge storage and transfer at electrified interfaces, and coupled transport of ionic and solvent species along pores or channels. Moreover, processes occur in confined spaces where the discrete nature of the system and its finite-size particles comes to the fore, determining equilibrium and nonequilibrium properties of the material. Dynamic deformation and structural alteration of electrochemical and biological media add further interesting facets to this picture. Both fields offer a virtually unlimited variety of structures and phenomena and, consequently, a wealth of possibilities to tune the properties and functionality of electrochemical devices and biological organisms. These phenomena are the focus of this seminar, organized along four main themes: stochastic and thermodynamic aspects of electrochemical and biological media, interfacial phenomena, soft biomaterials, and nanofluidics. The mix of experts and aspiring researchers from physical electrochemistry, biophysics, and soft matter physics stimulates a vivid exchange of ideas, with the goal to foster the formation of new cross-disciplinary partnerships. Understanding how nature has shaped biological matter will help inspire, design and build functionally optimized electrochemical materials and devices from the bottom up. In turn, advances in electrochemistry may inform the development of new materials for biological and medical applications.

Scientific Organizers:

Prof. Peter Berg

University of Alberta, Canada

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Prof. Barbara Wagner

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Introduction

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Venue:

Online via MeetAnyWay

Program (CET time)

Sunday, 09 May 2021

4:00 pm – 4:15 pm Peter Berg **Welcome address**
 Michael Eikerling
 Barbara Wagner

Setting the Stage - *Chair: Peter Berg and Michael Eikerling*

4:15 pm – 5:15 pm Narayana Aluru **Fluids in extreme confinement**

5:15 pm – 6:15 pm Alexei Kornyshev **Electrochemical nanophotonics -
using "ionics" for tuning photonic
functionalities of optical
metamaterials in real time**

Monday, 10 May 2021

Soft biomaterials – *Chair: Barbara Wagner*

9:00 am – 9:40 am David Andelman **Charge regulation in colloid
solutions and polyelectrolytes**

9:40 am – 10:20 am Matthew
Hennessy **Thermodynamically driven
instabilities in polyelectrolyte gels**

10:20am – 11:00 am Karin Jacobs **Biofilm adhesion: Interplay of
intermolecular forces between
surfaces and proteins or bacteria**

11:00 am – 12:00 am *COFFEE break & Networking opportunity*

Program (CET time)

Monday, 10 May 2021

Soft biomaterials – Chair: Barbara Wagner

12:00 pm– 12:40 pm	Anna Marciniak-Czochra	Mathematical modelling and model selection for pattern formation in developmental biology
12:40 pm– 1:20 pm	John King	Multiphase modelling of tissue growth
1:20 pm – 3:00 pm	<i>LUNCH break</i>	
3:00 pm – 4:00 pm	Networking	
4:00 pm – 4:10 pm	Stefan Jorda	About the WE-Heraeus-Foundation

Nanofluidics – Chair: Peter Berg

4:10 pm – 4:50 pm	Lyderic Bocquet	Iontronics in 1D and 2D nanomaterials
4:50 pm – 5:30 pm	Rene van Roij	A few short stories on iontronics
5:30 pm – 6:10 pm	Zuzanna Siwy	Ionic selectivity of nanopore transport and gating

Program (CET time)

Tuesday, 11 May 2021

Nanofluidics - Chair: Rene van Roij

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|--------------------|---------------------|---|
| 8:30 am– 9:10 am | Jürgen Fuhrmann | Quality preserving numerical methods for electrolyte modeling |
| 9:10 am – 9:50 am | Nir Gavish | Poisson-Nernst-Planck Lennard-Jones and high-order steric Poisson-Nernst-Planck models |
| 9:50 am – 10:15 am | <i>COFFEE break</i> | |

Posters – Chair: Barbara Wagner

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|---------------------|--|--|
| 10:15 am – 11:00 am | Poster soundbites I (3 slides / 3 min each) | |
| 11:00 am – 12:15 pm | Poster session I | |
| 12:15 pm – 1:00 pm | <i>LUNCH break</i> | |

Stochastic and thermodynamic aspects of biological and electrochemical media at the nanoscale – Chair: Peter Berg

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|-------------------|--|--|
| 1:00 pm – 1:40 pm | Benjamin Lindner | Linear and nonlinear fluctuation-dissipation theorems in non-equilibrium systems |
| 1:40 pm – 2:20 pm | Serge Lemay | Local electrokinetics driven by electrochemistry |
| 2:20 pm – 3:00 pm | Roland Netz | Electrokinetics at biological surfaces: Ion-specific adsorption, local viscosity and dielectric effects |
| 3:00 pm – 4:00 pm | <i>COFFEE break & Networking opportunity</i> | |
| 4:00 pm – 4:40 pm | Aimy Bazylak | Examining multiphase flows in fuel cells and electrolyzers |
| 4:30 pm – 5:20 pm | David Sivak | Nonequilibrium energy transduction is maximized for flexibly linked machine components |

Program (CET time)

Wednesday, 12 May 2021

Interfacial phenomena: electrocatalysis to complex media -

Chair: Michael Eikerling

8:30 am – 9:10 am	Karen Chan	"pH effects" in electrocatalysis
9:10 am – 9:50 am	Axel Groß	Modelling interfacial structures and processes in electrochemical energy storage and conversion
9:50am – 10:30 am	Jun Huang	Orbital-free density-potential functional theory of electric double layer
10:30 am – 11:00 am	<i>COFFEE break</i>	
11:00 am– 11:40 am	Katharina Krischer	Electrochemical many-particle systems with coexisting states
11:40 am– 12:20 pm	Birger Horstmann	SEI Growth on Graphite and Silicon Electrodes
12:20 pm – 1:00 pm	<i>LUNCH break</i>	

Posters – Chair: Michael Eikerling

1:00 pm – 2:15 pm	Poster soundbites II (3 slides / 3 min each)	
2:15 pm – 3:45 pm	Poster session II	
3:45 pm – 4:30 pm	<i>COFFEE break</i>	
4:30 pm – 5:45 pm	Thematic discussion (centered around main themes in breakout groups)	
5:45 pm – 6:00 pm	Peter Berg Michael Eikerling Barbara Wagner	Poster awards, summary, closing remarks, outlook

End of the seminar

Posters

Posters Tuesday

- 1** Yael Avni **Charge-regulated macro-ions in ionic solutions**
- 2** Yongting Chen **pH Effect of MN4-C catalysts for oxygen reduction under fix-potential**
- 3** Oskar Cheong **Ethanol dehydrogenation on supported platinum-based catalyst studied by ab initio calculations**
- 4** Mehrtoos Eslamibidgoli **Ab initio study of NiOOH (0001) surfaces: Deprotonation and alkali metal cation adsorption**
- 5** Evgenii Fedorov **Accelerated force field development using active learning: The case of advanced electrolytes for Li-ion batteries**
- 6** Jasmin Kaur **Physics-based impedance model to diagnose pore-level effects in PEFC electrodes**
- 7** Peng Li **Establishment of the potential of zero charge of metals in aqueous solutions: Different faces of water revealed by ab initio molecular dynamics simulations**
- 8** Rebekka Tesch
Bart Verlinden **Computation of solvent effects in electrochemical and organic systems**
- 9** Bin Zheng **Phase separation of polyelectrolytes: The effect of charge regulation**

Posters Wednesday

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| 10 | Ana Maria Gomez Marin
Andrii Koverga | Rational design of catalytic surfaces for fuel cell technologies by selective molecular patterning |
| 11 | Svenja Hövelmann | X-ray studies of dynamics of photoswitchable lipid membranes |
| 12 | Henrik Kristoffersen | Towards constant potential modeling of CO-CO coupling at liquid water-Cu(100) interfaces |
| 13 | Sihang Liu | Theoretical studies of furfural electroreduction on copper electrode |
| 14 | Thomas L. Maier | Boosting hydrogen evolution reaction by lateral electrode structuring |
| 15 | Ricardo Martinez Hincapie | Interfacial pK₂ of carbonic acid at the Pt(hkl)/solution interface |
| 16 | Alexandre Pereira dos Santos | Electroosmotic flow grows with electrostatic coupling in confining charged dielectric surfaces |
| 17 | Paul Robin | Building a theoretical prototype of a Hodgkin-Huxley neuron using 2D nanofluidic memristors |
| 18 | Olga Sambalova | Magneto-optical probing of magnetic-field facilitated electrochemical hydrogen evolution enhancement |
| 19 | Sudarshan Vijay | Ab-initio electrochemical kinetics simulation methodology coupled to continuum models for describing trends in the oxygen reduction reaction |
| 20 | Martin Werres | Modelling of lithium droplet formation during lithium dissolution |

Posters Wednesday

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| 21 | Yun-Chiao Yao | Carbon nanotube porins: Bio-compatible nanofluidic circuitry |
| 22 | Yufan Zhang | Criterion for finding the optimal electrocatalyst at any overpotential |
| 23 | Xinwei Zhu | Origins of potential dependent tafel slope of electrochemical CO₂ reduction on silver |

Abstracts of Talks

(in alphabetical order)

Fluids in Extreme Confinement

N. R. Aluru

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When the size of the fluid molecule is comparable to the size of the channel or pore through which the fluid is transported, the fluid is under extreme confinement. At these length scales, many interesting issues arise and classical definitions need to be revisited. This talk focuses on highlighting some of the fundamental aspects that need to be considered at these length scales. In particular, we show the importance of quantum coupling between the fluid and the solid, selective transport of fluid molecules via conformational changes and the importance of pore/membrane conformational changes for ultrathin materials.

References

- [1] Qu et al., Nat Comm **12**, 310 (2021)
- [2] Noh and Aluru, ACS Nano **14**, 10518 (2020)

Charge Regulation in Colloid Solutions and Polyelectrolytes

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²UCAS and IOP, Chinese Academy of Sciences, Beijing, China

The phenomenon of **charge regulation** was introduced by Ninham and Parsegian 50 years ago and was successfully applied in many studies to charged surfaces in contact with an electrolyte. We revisit the charge-regulation mechanism within the Poisson-Boltzmann theory and apply it to mobile macro-ions in a bathing salt solution. First, we examine the effects of correlation between various adsorption/desorption sites in terms of an effective Debye screening length, which can exhibit a non-monotonous behavior as a function of system parameters. Furthermore, we demonstrate that above a critical concentration of salt, similar to the critical micelle concentration, a non-trivial distribution of charge states sets in. Such a charge state can eventually lead to a liquid-liquid phase separation based on charge regulation. Finally, we apply the mechanism of charge regulation to phase separation of solutions of oppositely charged polyelectrolytes (known as **complex coacervation**). It is shown that during the phase separation, the polymers in the condensed phase are more charged than in the dilute phase, in accord with Le Chatelier's principle.

References

- [1] B. Zheng, Y. Avni, D. Andelman, and R. Podgornik, submitted to *J. Phys. Chem. B* (2021).
- [2] Y. Avni, R. Podgornik, and D. Andelman, *J. Chem. Phys.* **153**, 024901 (2020).
- [3] Y. Avni, D. Andelman, and R. Podgornik, *Curr. Opin. Electrochem.* **13**, 70 (2019).
- [4] Y. Avni, D. Andelman T. Markovich, and R. Podgornik, *Soft Matter* **14**, 6058 (2018).

Examining multiphase flows in fuel cells and electrolyzers

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Energy storage is a vital for energy security as well as water security, yet energy storage is hugely lacking around the world. Fortunately, energy storage can be realized through the combination of fuel cells and electrolyzers; however, key challenges for these technologies must be overcome to make way for widespread implementation. Polymer electrolyte membrane (PEM) fuel cells and electrolyzers are composed of porous materials, including the catalyst layer, microporous layer, and substrate. Available materials typically exhibit highly heterogeneous material and chemical properties. To reach cost targets for widespread commercial adoption, materials must enable more effective multiphase flow phenomena than what currently exists. Mass transport losses in PEM fuel cells and electrolyzers are both prohibitively significant, yet designing these materials requires the a priori knowledge of how the heterogeneous properties of the porous materials and their interfacial contacts influence electrochemical performance. I will discuss the critical design factors (heterogeneous porous materials and nature of interfacial contacts) and how they influence the flow and mass transport behaviour in PEM fuel cells and electrolyzers. I will also discuss the new materials we have designed and fabricated, informed by in-house numerical modelling and tested through a combination of in operando and ex situ X-ray and neutron beam characterization approaches.

Iontronics in 1D and 2D nanomaterials

Lydéric Bocquet,
Ecole Normale Supérieure and CNRS,
<http://www.phys.ens.fr/~lbocquet/>

Nature does many exquisite things with ions and fluids at small scales, and in a very efficient way. Mimicking some of its functionalities in artificial devices would be tremendous, for example to design new energy-efficient computation architectures based on ions rather than electrons. In the emerging nanofluidic field, there has been considerable progress recently in the design and study of transport in channels at nanoscales. These artificial systems still remain far from the impressive complexity of the biological machinery. However, a wealth of interesting far from equilibrium and many-body behaviours have been revealed, which constitute building blocks to build such advanced functionalities.

In this talk, I will report on our recent progress in 1D and 2D iontronics, involving experiments and theory of water and ion transport across carbon nanotubes and 2D (sub)nanometer slits made of van der Waals heterostructures. I will report on the strongly non-linear transport properties across these 1D and 2D. This includes voltage gating and pressure-dependent conductance, which closely mimics the response of biological (Piezo) mechano-sensitive ion channels.

Beyond, we predict how the peculiar ion transport in 2D nanometric channels leads to a memristor behaviour with a history-dependent conductivity. Such a device allows us to reproduce the Hodgkin-Huxley neuron model in a 2D nanoslit and a simple circuitry highlights spontaneous emission of voltage spikes trains characteristic of neuromorphic activity. I will show that memristive behavior is indeed highlighted experimentally in the 2D systems, allowing to design the basic functions of a synapse with elementary 'learning' functionality using the nanofluidic circuitry.

References:

- "Mechanically activated ionic transport across single digit carbon nanotubes", A. Marcotte, T. Mouterde, A. Nigues, A. Siria and L. Bocquet, **Nature Materials**, **19**, 1057–1061(2020)
- "Molecular streaming and voltage-gated response in Angström scale channels" T. Mouterde, A. Keerthi, A. Poggioli, S. Dar, A. Siria, A.K. Geim, L Bocquet and R. Boya, **Nature** **567** 87 (2019)
- "Ionic Coulomb blockade as a fractional Wien effect" N. Kavokine, S. Marbach, A. Siria, L. Bocquet, **Nature Nanotechnology** (2019)
- "Hodgkin-Huxley iontronics with two-dimensional nanofluidic memristors", P. Robin, N. Kavokine, and L. Bocquet, under review (2021)

“pH effects” in electrocatalysis

Karen Chan²

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²*another Institute, another town, another country*

Beyond surface reaction energetics, the structure and composition of the electric double layer exerts an influence on the activity and selectivity of electrochemical reactions. These phenomena often manifest themselves as so-called “pH effects”, which manifest as deviations in the dependence of activity from a potential vs. RHE scale. In this talk, I first discuss the impact of the electrolyte on electrocatalytic activity from the perspective of the impact of the proton donor and adsorbate dipole-field interactions, as well as how cations and supported single site catalysts tune the latter. I then discuss the impact of solution phase reactions and mass transport on activity and selectivity. I draw examples from hydrogen evolution and electrochemical CO₂ reduction, and discuss the implications of fundamental mechanistic understanding on catalyst design.

References

- [1] Resasco, Chen, Clark, Tsai, Hahn, Jaramillo, Chan, Bell, *JACS*, 2017
- [2] Ringe, Morales-Guio, Chen, Jaramillo, Hahn, Chan, *Nature Communications*, 2019
- [3] Vijay, Gauthier, Heenen, Bukas, Kristoffersen, Chan, *ACS Catalysis* 2020
- [4] Ringe, Clark, Resasco, Walton, Seger, Bell, Chan *Energy. Env. Sci.* 2019
- [5] K. Chan, *Nature Comm.*, 2020

Quality preserving numerical methods for electrolyte modeling.

J.Fuhrmann¹

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We present a finite volume method for the discretization of ion drift and diffusion in a self-consistent electric field for an electrolyte in mechanical equilibrium which adapts discretization techniques developed for semiconductor devices. The underlying ion transport model is based on a generalized Nernst-Planck-Poisson model which takes into account finite ion size and solvation effects. We give an overview on thermodynamic consistency and convergence results for the method.

A straightforward extension of the model to nanoscale electroosmotic flows involves the coupling to the incompressible Navier-Stokes equations. For this purpose, the finite volume method for ion transport is combined with a pressure robust finite element discretization method for the flow. This method has the advantage to preserve the divergence constraint on the discrete level, allowing to prevent unphysical concentration fluctuations in the coupling process.

We present numerical simulation examples for electrolytes and electroosmotic flows at the nanoscale confirming the validity and the advantages of the discretization approach.

References

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- [2] M. Landstorfer, C. Gohlke, W. Dreyer. *Electrochim. Acta* **201** 187-219 (2016)
- [3] J. Fuhrmann. *Fuel Cells* **16(6)** 704–714 (2016)
- [4] J. Fuhrmann, C. Gohlke, A. Linke, C. Merdon, R. Müller. *Electrochim. Acta*, **317**, 778–785 (2019)
- [5] B. Gaudeul, J. Fuhrmann. DOI: 10.20347/WIAS.PREPRINT.2811 (submitted)

Poisson-Nernst-Planck Lennard-Jones and high-order steric Poisson-Nernst-Planck models

Nir Gavish¹

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The Poisson-Nernst-Planck-Lennard-Jones (PNP-LJ) model is a mathematical model for ionic solution with Lennard-Jones interactions between the ions. Due to the singular nature of the Lennard-Jones interaction kernel, however, the PNP-LJ model gives rise to an intractable analytic problem and a highly demanding computational problem. Previous works tackled this problem by replacing the LJ potential with a leading order approximation of the LJ potential giving rise to the steric PNP model. The steric PNP proved to be a successful model for the transport of ions in biological ionic channels. However, in important parameter regimes, it is ill-posed.

In this talk, we present a study that goes beyond the leading order approximation of the Lennard-Jones (LJ) interaction kernel, and develops a new class of high-order steric PNP equations. Surprisingly, we show that the introduction of high-order terms does not regularize the steric PNP model. Namely at the limit of vanishing ionic sizes, high-order steric PNP equations, at all orders including the PNP-LJ model, are ill-posed at important parameters regimes. Further analysis shows that this is an inherent property of PNP equations which accounts for steric effects and is related to pattern formation in these systems.

Modelling interfacial structures and processes in electrochemical energy storage and conversion

Axel Groß^{1,2}

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²*Helmholtz Institute Ulm, 89081 Ulm/Germany*

Structures and processes at electrochemical electrode/electrolyte interfaces play a critical role in our future energy storage and conversion technology based on, e.g., batteries and fuel cells. However, from a modelling perspective the atomistic description of electrochemical interfaces is challenging, in particular for liquid electrolytes, as a proper treatment in principle requires quantum chemical approaches together with an appropriate statistical sampling of the liquid electrolyte (see Fig. 1) [1,2]. In this contribution, I will present recent attempts to model electrochemical interfaces relevant in electrocatalysis and metal-air batteries using ab initio molecular dynamics simulations [1,2], classical MD simulations [3] and grand-canonical approaches [4], also taking ions present in the aqueous electrolytes appropriately into account.

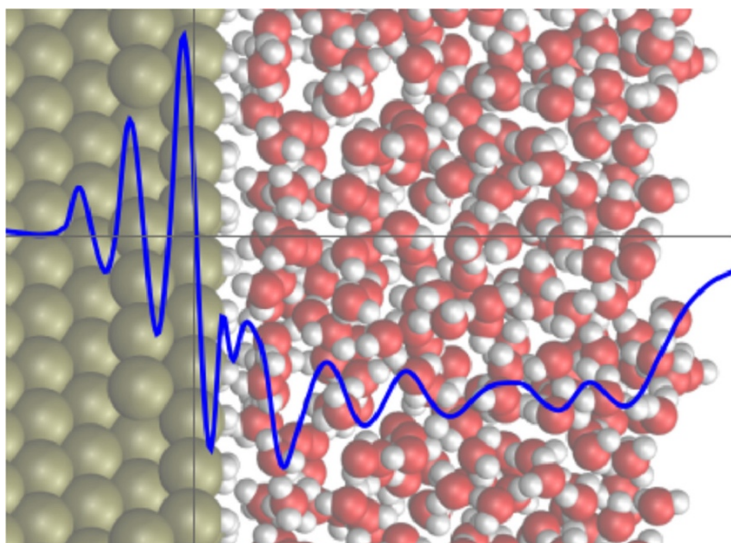


Fig. 1: Snapshot of a ab initio molecular dynamics simulations of a water/Pt(111) interface together with an averaged one-electron potential change (full line) [1].

References

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- [2] Sung Sakong and Axel Groß, *J. Chem. Phys.* **149**, 244105 (2018).
- [3] A. Sergeev et al., *J. Phys. Chem. C* **121**, 22659 (2017).
- [4] F. Gossenberger, F. Juarez, A. Groß, *Front. Chem.* **8**, 634 (2020).

Thermodynamically driven instabilities in polyelectrolyte gels

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Polyelectrolyte gels are soft, two-phase materials consisting of a network of electrically charged polymer chains that are swollen with an ionic solution. Slightly altering the temperature or ionic concentration of the surrounding aqueous environment can trigger thermodynamic instabilities that drive a wealth of fascinating behaviours such as discontinuous changes in the gel volume and the self-assembly of complex structures within and on the surface of the gel. To elucidate the origin of these dynamic behaviours, we have developed a thermodynamically consistent model of a polyelectrolyte gel that accounts for the large deformations of polymer chains, free energy of diffuse internal interfaces, and electrostatic interactions between charged species [1]. An analysis of the electric double layer at the gel-bath interface reveals that the gel can separate into a periodic structure consisting of alternating layers that are rich in either anions or cations [2]. Numerical simulations in 1D show that the evolution between equilibrium states occurs via travelling waves and/or the formation of slowly coarsening localised structures, both of which can result in experimentally visible patterns [3] that may be relevant to the design of stimuli-responsive smart materials and organelle formation in biological cells.

References

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- [2] M. G. Hennessy et al, WIAS Preprint **2751** (2020)
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SEI Growth on Graphite and Silicon Electrodes

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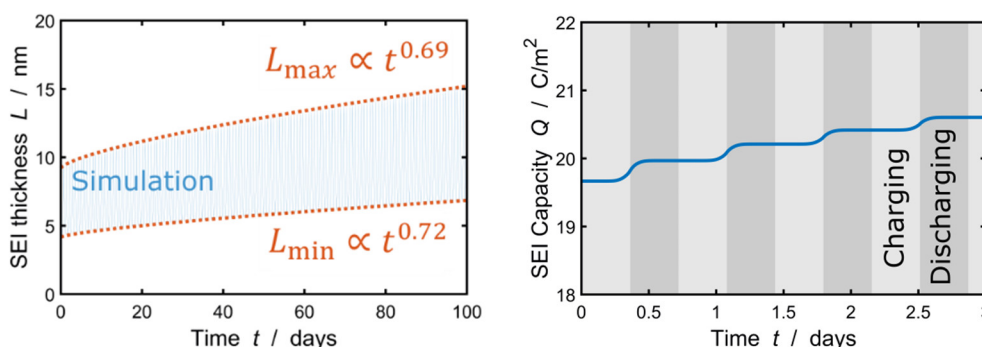
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Electrolyte reduction products form the solid-electrolyte inter-phase (SEI) on negative electrodes of lithium-ion batteries. Even though this process practically stabilizes the electrode-electrolyte interface, it results in continued capacity-fade limiting lifetime and safety [1]. Most SEI models focus on capacity fade as a function of time. By modelling additional properties and dependencies, our recent continuum theories give new insights into the growth and deformation of SEI structure and its function [2,3].

We give arguments that the diffusion of neutral radicals limits the growth of SEI thickness [4], as it predicts the observed potential dependence of SEI growth [5]. 3D micro-structure resolved simulations show that this potential dependence results in SEI inhomogeneity throughout the negative electrode. We extend this calendar-life model to describe the observed asymmetry in SEI growth during battery operation [6] and validate it with recent experiments of differential capacity loss during cycling [7].

Silicon as material for negative electrodes offers high theoretical energy densities. Unfortunately, it exhibits a large volume change during lithium intercalation. This exerts stress on the SEI, leads to continued SEI fracture, and constitutes a major source for capacity fade of silicon anodes. We present a combined mechanical and electrochemical theory of silicon electrodes which captures SEI growth, elastic deformation, plastic flow, and cracking during battery cycling. In this way, we study the evolution of SEI structure during cycling of silicon electrodes.

This work is supported by the German Research Foundation (DFG) via the research training group SIMET.



References

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Orbital-Free Density-Potential Functional Theory of Electric Double Layer

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The Kohn-Sham density functional theory (KS-DFT) treats the electronic structure problem using an implicit density functional for the kinetic energy and an explicit approximation for the exchange-correlation energy. The kinetic energy has to be calculated self-consistently by enumerating all orbitals, which renders the computational cost too high for large systems (i.e. $>10^2$ atoms). Therefore, KS-DFT is difficult to simulate the electric double layers (EDL), which are typically several nm thick. Another well-known challenge arises from the fact that the EDL is a grand-canonical, electrified system. Last but not least, it is hard to adequately sample the solvation configurations. Many have been attempting at tackling the named challenges using various modifications based on the KS-DFT, see a recent review [1].

Here, we present an alternative approach [2,3], which uses explicit approximations for both kinetic and exchange-correlation functionals, and a free energy functional for the electrolyte solution that is derived rigorously from statistical field treatment and exact at the mean-field level. This way, an orbital-free density-potential functional that encompasses major effects in the contacting metal and electrolyte phases can be formulated. Variational analysis of this functional yields a grand-canonical model of the EDL. The present approach is able to simulate large-scale EDLs, accounting for essential quantum mechanical and classical effects at the cost similar to the classical Gouy-Chapman-Stern model, because we do not need to calculate orbitals any more.

In this talk, I will discuss the philosophy, the construction, preliminary applications, and future tasks of the approach.

References

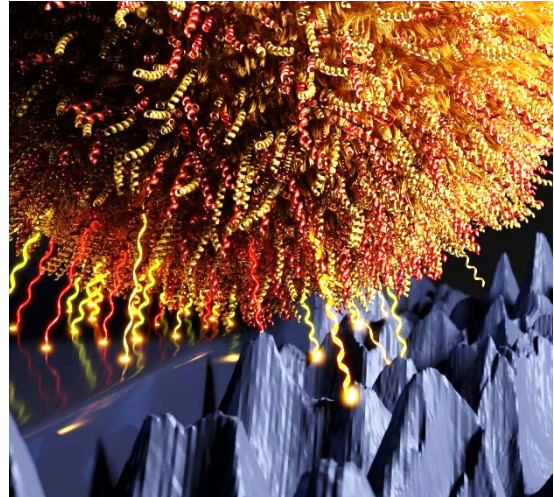
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Biofilm adhesion: Interplay of intermolecular forces between surfaces and proteins or bacteria

Karin Jacobs¹

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Microbial biofilms are common in everyday life, which, however, may constitute serious health problems, especially in the hospital setting. In order to establish a biofilm on organic or abiotic surfaces, microbes first need to attach to these surfaces. In this project, atomic force microscopy based single cell force spectroscopy (SCFS) is used to study the basic principles of proteinaceous and microbial adhesion on biotic/abiotic surfaces in aqueous solutions, and the impact of host factors on this process. In a collaboration with theoretical physicists (L. Santen, U Saarland), we aim to determine the microscopic mechanisms that govern the dynamical evolution of selected protein and bacterial biofilms [1].



Our recent findings show that adhesion of microbes to abiotic surfaces is mainly driven by hydrophobic/hydrophilic interactions between the surface and the extracellular protein contents of the microbes, the (nano-) structure of the surface, and surface decoration by host factors [2, 3, 4]. MC simulations of our collaborators help to interpret the observed force/distance curves recorded by SCFS.

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Multiphase modelling of tissue growth

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Some simple partial-differential equation models for biology tissue growth will be described, and some of their properties elucidated. While the models in question are of macroscale type, the way multiscale (cellular and sub-cellular) processes are reflected therein will be noted.

Electrochemical Nanophotonics

Using “ionics” for tuning photonic functionalities of optical metamaterials in real time

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This talk will overview a new direction of research that can be conventionally called “electrochemical photonics”, the main task of which is creation on novel kind of optical metamaterials, the functionalities of which can be tuned in real time.¹ It is based on voltage-controlled self-assembly of plasmonic nanoparticles at electro-chemical liquid-liquid or solid-liquid interfaces, the optical properties of which can dramatically vary with assembly structure and density. The effects to be discussed were predicted by theory and have been, navigated by theory, experimentally realized by a team at Department of Chemistry of Imperial; these refer to electro-switchable window-mirrors, tuneable colour mirrors, Fabry-Perot cavity filters, new scenarios for enhanced extraction of light from LED displays, as well as ultrasensitive detectors of hazardous molecules or pollutants using novel self-assembling and tuneable plasmonic platforms.

¹For latest min-review see: A.A. Kornyshev, Electrochemical metamaterials, *J. Solid State Electrochem.* **24**, 2101-2111 (2020).

Electrochemical Many-Particle Systems with Coexisting States

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Bistability, i.e. the coexistence of different states at identical external parameters, is a frequently encountered phenomenon in electrode reactions. If the reactions occur on individual catalytically active areas that are all electrically connected, each active area can be considered as a bistable component, and the entire ensemble as a many-particle system of such interconnected bistable components. Examples range from (micro-)electrode arrays, where the individual electrodes constitute the bistable components, to insertion battery cathodes, where each of the billions of nano-particulate storage particles can be considered a bistable component.

In this talk, we will first introduce a general mathematical description of bistable many particle systems and compile key results [1]: (1) All steady states are composed of one, two or three clusters. (2) Stable steady states possess at most one electrode on the intermediate, autocatalytic branch. (3) Ensembles of globally coupled bistable components might exhibit oscillations. We will derive a necessary condition of when the system might become oscillatory. In the second part, the model will be applied to different electrochemical systems, such as the oxidation of CO on coupled Pt electrodes, or Li insertion batteries

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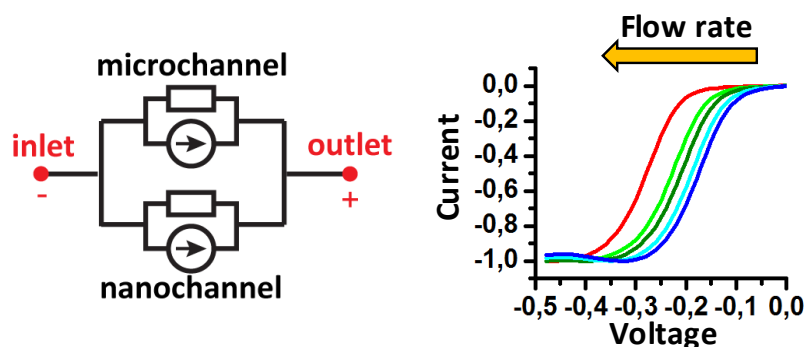
Local electrokinetics driven by electrochemistry

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Fluid and charge transport in micro- and nanoscale systems are intrinsically coupled via electrokinetic phenomena. While the influence of electroosmotic flows and streaming potentials is well understood for externally imposed driving forces, the impact of local charge injection by electrochemistry *inside* fluidic systems remains largely unexplored. We use microscale electrodes and nanogap electrode pairs to study the subtle interplay between ohmic drops, streaming currents and faradaic processes in miniaturized channels at low supporting electrolyte concentrations. Electroosmosis can, under favorable circumstances, counteract the effect of ohmic losses and shift the apparent formal potential of redox reactions, leading to seemingly ‘nonlocal’ interactions between different parts of a network [1]. Conversely, charge injection can generate local convection, drastically altering the trajectories of microparticles in so-called impact electrochemistry assays [2]. These observations help understanding a number of unexplained observations in electrochemical fluidics.



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Linear and Nonlinear fluctuation-dissipation theorems in non-equilibrium systems

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Many small systems in physics and biology display irregular (noisy) behavior, which can be well described in a stochastic framework. In equilibrium systems the characteristics of spontaneous fluctuations and the characteristics of the linear response to external perturbations are connected via well-known fluctuation-dissipation theorems (FDT). If we experimentally (say, in a biological system like the sensory hair bundle) observe a violation of such an equilibrium FDT, this can be regarded as a model-free proof that the system is out of equilibrium [1]. However, there are also more generalized fluctuation-dissipation theorems [2] that compare the spontaneous fluctuations and the linear response for a suitably transformed variable and find that the two are related even in a nonequilibrium situation if the system obeys Markovian dynamics (experimental confirmation for the sensory hair bundle e.g. in [3]). Hence, if this kind of theorem is violated, it indicates that the system is non-Markovian (at least in the set of observed variables). In this talk I show that the practical application of this test-of-Markovianity idea by a linear nonequilibrium FDT is seriously limited by the required amount of experimental data [4]. I discuss a nonlinear version of the theorem that requires fewer data but a specific perturbation and measurement protocol. This nonlinear FDT is tested on simple nonequilibrium Markovian and non-Markovian models and the results are discussed.

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Mathematical modelling and model selection for pattern formation in developmental biology

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Cells and tissues are objects of the physical world, and therefore they obey the laws of physics and chemistry, notwithstanding the molecular complexity of biological systems. A natural question arises about the mathematical principles at play in generating such complex entities from simple laws. In this talk, I show how different pattern formation concepts may stand challenges arising from the current experimental research. Specifically, Turing-style morphogen-based models are compared to mechano-chemical models exhibiting de novo pattern formation. Patterning potential of mechano-chemical interactions is investigated using two classes of mathematical models coupling dynamics of diffusing molecular signals with a model of tissue deformation. The first class of models is based on energy minimization that leads to 4-th order partial differential equations of evolution of infinitely thin deforming tissue (pseudo-3D model), coupled with a surface reaction-diffusion equation. The second approach (full-3D model) consists of a continuous model of large tissue deformation coupled with a discrete description of spatial distribution of cells to account for active deformation of single cells. Different mechanisms of pattern formation will be compared using Bayesian calibration methods [3].

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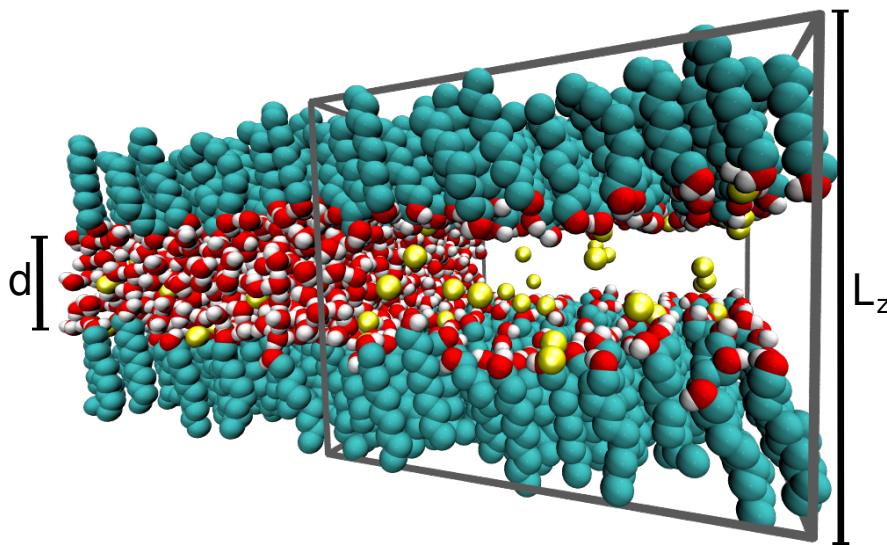
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Electrokinetics at biological surfaces: Ion-specific adsorption, local viscosity and dielectric effects

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The ζ -potential of mineral and biological surfaces is used to characterize the specific surface affinity of ions. The non-vanishing ζ -potential of zwitterionic net-neutral phospholipid vesicles in neat water is consistently observed in experiments but not fully understood theoretically. Using atomistic molecular dynamics simulations in combination with the modified Poisson-Boltzmann equation, we study the dielectric and viscous properties of various aqueous interfaces and specific ion-surface interactions. We quantitatively reproduce and explain experimental results for the ζ -potential. For lipid membrane surfaces we need to postulate minute amounts of surface-active anionic impurities in lab water and also in the added salt.



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Nonequilibrium energy transduction is maximized for flexibly linked machine components

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Living systems at the molecular scale are composed of many constituents with strong and heterogeneous interactions, operating far from equilibrium, and subject to strong fluctuations. These conditions pose significant challenges to efficient, precise, and rapid free energy transduction, yet nature has evolved numerous biomolecular machines that do just this. What are the physical limits on such nonequilibrium performance, and what machine designs actually achieve these limits? In this talk, I discuss a simple model of the ingenious rotary machine that makes ATP (the predominant portable energy currency of the cell), where one can investigate the interplay between nonequilibrium driving forces, thermal fluctuations, and the strength of interactions between strongly coupled subsystems. This model reveals nontrivial yet intuitive design principles for effective molecular-scale free energy transduction. Most notably, while tight coupling between machine components is intuitively appealing, output power is in fact maximized at intermediate-strength coupling, which permits lubrication by stochastic fluctuations with only minimal slippage.

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Ionic selectivity of nanopore transport and gating

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Nanopores with tunable geometry and electrochemical properties of the pore walls serve as a template to understand ionic and molecular transport at extreme confinement. Due to nanoconfinement, nanopores can exhibit ionic selectivity, i.e. the ability to transport only one type of ions, nonlinear current-voltage characteristics, and ion current switching behavior, among others. In the talk, I will present design principles for nanopores that are selective for one type of ion. An example of a nanopore that selectively transports potassium ions but does not transport sodium ions will be shown.^[1] I will also describe transport properties of hydrophobic nanopores, specifically, how hydrophobic gating can be controlled by the type of ion, ionic concentrations,^[2] and presence of local charges.^[3] Perspective on using nanopores as model systems to uncover electrochemical properties of unknown solid/liquid interfaces will be discussed as well.^[4,5]

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A few short stories on iontronics

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Fluid flow in channels and through pores can have a profound effect on the surface charge and on the chemical equilibria on the surface [1,2]. In this talk we will discuss and solve (modified) Poisson-Nernst-Planck-Stokes equations for conduction-advection-diffusion processes in aqueous electrolytes, coupled to adsorption-desorption equilibria of ions on the surface walls (charge regulation). We will see that the fluid flow tends to generate lateral gradients on otherwise homogeneous surfaces, such that chemical equilibria may vary spatially between the inlet and the outlet of a channel [3]. In particular, the surface charge density and the dissolution rate may vary spatially upon applying a flow. We will also touch upon the remarkably interesting information on the ion valency, the reaction mechanism, and the reaction rates that can be obtained from surface charge relaxation processes from initially overcharged and undercharged surfaces [4]. Finally, if time permits, we will discuss some peculiar transport properties of fluid and charge through cone-like channels [5].

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Abstracts of Posters

(in alphabetical order)

Charge-regulated macro-ions in ionic solutions

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Macromolecules in aqueous environments often carry an unfixed charge due to the dissociation/association of their ionizable groups. The degree of dissociation/association is coupled to the local electrostatic potential, allowing for *Charge Regulation* to occur, and modifying the present electrostatic interactions. We formulate a mean-field theory to describe mobile macro-ions in a bathing salt solution, taking into account the charge regulation of the macro-ions as internal degrees of freedom. The behavior of the macro-ionic solution is understood through its modified screening length that combines the standard screening due to the mobility of the macro-ions and salt, and an additional screening that stems from the freedom of the macro-ions to adjust their charge. The latter can cause the screening length to depend non-monotonically on the salt concentration.

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The activity coefficient of z:1 ionic solutions scales with the cube root of salt concentration

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The activity coefficient of ionic solutions was proposed to depend on the cube root of concentration in the early 20th century by Niels Bjerrum (1916) based on a good fit to data. No fundamental theory was presented at that time. A theory was later presented by Debye and Hückel (1923) proposing a square root dependence. The derivation of the DH theory is quite contrived and several approximate steps and fit parameters are required. And even at that time it was known that the cube root law gives a better fit to data than the DH theory. Also, over the decades the possible range of validity of the DH law was reduced to lower and lower concentrations, at some point no longer considered to be valid above for instance 0.1 mM salt concentration. Still the DH square-root law prevailed and is often taught in physical chemistry classes.

We propose the concept of an ion ensemble, which is as simple as an ion pair in case of a symmetric salt, and we analyze Coulomb's law for all possible configuration of the ions in the ion pair, or ion ensemble. An ion pair is an ion together with its closest counterion. The distribution of the likelihood of the distances between the ions in an ion pair first increasing from a very low probability for being very close, to a maximum, and from some distance onward, the probability of two ions being an ion pair drops precipitously, because for larger distances, ions are not likely an ion pair, because they will be paired up (in an ion pair) with other ions. Thus, when the salt concentration is increased, ion pairs are pushed together, but for solely statistical reasons!

For a 1:1 salt we derive an elegant formula for the activity coefficient that depends on the Bjerrum length and the cube root of salt concentration, without further fit parameters. It fits data for the activity coefficient perfectly well. The same general theory also fits data for 2:2 and 3:3 salts, but then there is no cube root relationship. The theory also works for 2:1 and 3:1 salts, then the data do show a cube root dependence but we have not yet found a way to derive this from the ion ensemble theory. The only fit parameter is the average ion size, and we derive very realistic values, unlike the aberrant ion sizes required in the DH theory. Note that the DH theory has a fundamental flaw as it only presents results for the (Helmholtz) energy per ion but does not go through the required steps to derive the contribution to the chemical potential (Gibbs energy). Already in the dilute limit this results in a 33% error.

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pH Effect of MN4-C catalysts for oxygen reduction under fix-potential

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Non-noble metal materials are promising catalysts for oxygen reduction reaction (ORR), among which transition metal (e.g. Fe) and nitrogen co-doped carbons (M-N-C) have attracted wide interest. M-N-C catalysts deliver an ORR activity of almost two orders of magnitude higher in acidic than alkaline media, which remains puzzling. Herein, the origins of this pH effect are investigated using density functional theory (DFT) based first-principles simulation. With iron phthalocyanine supported on graphene (G-FePc) as the model catalyst, the presented DFT study features a pH-dependent excess system charge, resulting in pH-dependent work function, adsorption energies of ORR intermediates, and the redox potential of Fe(II/III). Our results also show descending reaction energy barriers on increasing pHs from acidic to alkaline media among the M-N-C catalysts. The ORR rate determining step (RDS) of *H₂O desorption in acid transforms into *OOH formation in alkali. Our work provides a fundamental understanding of the charge/pH effects in non-noble metal catalysts, calls for re-evaluation of the previously suggested mechanisms by including the overlooked electrochemical constant-potential effects.

Ethanol dehydrogenation on supported platinum-based catalyst studied by ab initio calculations

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In the on-going transformation of the energy economy, ethanol is emerging as a renewable feedstock that can be further catalytically processed to various organic intermediates and products such as acetaldehyde, ethylene, methane, hydrogen and other compounds. In order to improve the fundamental understanding of ethanol dehydrogenation on metal catalysts, we have performed combined theoretical and experimental studies of ethanol dehydrogenation on a Pt/C catalyst. Using Density Functional Theory (DFT) we have computed parameters of the underlying chemical reactions, including adsorption energies and activation barriers. Having obtained these parameters, we are able to delineate dehydrogenation pathways that have been proposed to explain experimentally observed trends in the catalytic selectivity for H₂ and CH₄ formation [1]. We discuss how a combination of atomistic simulations and experimental analyses contributes to understanding catalytic processes of simple organic compounds on metallic catalysts.

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***Ab initio* Study of NiOOH (0001) Surfaces: Deprotonation and Alkali Metal Cation Adsorption**

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Nickel-based oxides are highly active, cost effective materials for the oxygen evolution reaction (OER) in alkaline conditions. Recent experimental studies have revealed the importance of surface deprotonation and alkali metal cation adsorption on the OER activity of Ni oxide surfaces, in contact with aqueous alkaline electrolyte [1,2]. In this study, we employ the DFT+U method within the grand-canonical scheme based on the computational hydrogen electrode [3] to determine the stable interface structure of β -NiOOH (0001) under varying electrochemical conditions (pH and electrode potential). We will discuss the effect of surface water layer and the potential-dependent shift in Gibbs free energy of adsorption arising from the interaction of surface dipoles with the interfacial electric field on the computed surface Pourbaix diagrams.

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Accelerated force field development using active learning: the case of advanced electrolytes for Li-ion batteries

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Molecular dynamics (MD) simulations with accurate and validated force fields are very useful in understanding poorly known correlations between type and composition of ingredients during fabrication of Li-ion battery electrodes. Although computationally efficient, these models have limited accuracy and transferability due to tens to hundreds of parameters to tune depending on the functional form of the force fields. This task of optimization is usually challenging and highly time-consuming, and to make it more efficient and autonomous, one can use machine learning (ML) algorithms. For that, the algorithm uses experimental data and/or high-fidelity simulations as a reference, bridging the gap between the different scales and the MD simulations. This project makes use of Bayesian Optimization (BO) coupled with Gaussian Process Regression (GPR). It will iteratively predict the performance and the uncertainty of a given set of parameters (GPR) and select a new datapoint in the parameter space as an exploration vs. exploitation trade-off (BO). The simulated systems are EC/LiP6 and DMC/LiPF6 performed using Buckingham and OPLS-AA potentials. Ab-initio simulations and experimental data are extracted from papers, which serve as the references. The developed autonomous framework for parameterization is expected to make the tuning process easier and computationally efficient.

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X-ray studies of dynamics of photoswitchable lipid membranes

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For potential health science applications such as drug delivery, one interesting approach is to alter structure and interfacial tension in phospholipid membranes by embedding photoswitchable molecules. Understanding the dynamics of such photo-induced modifications is also of fundamental interest. Therefore, we investigate a 1,2-dipalmitoyl-phosphatidylcholine (DPPC) Langmuir film with embedded photoswitchable azobenzene-glycolipid molecules as a model system. We use multiple measurement techniques to characterise the structural changes, their evolution and time scales with absorption spectroscopy, Langmuir isotherms, X-ray reflectivity and grazing incident X-ray diffraction. The azobenzene-glycolipids switch reversibly between their trans- and cis-conformation by illumination with UV and blue light and induce a reversible structural change in the membrane they are embedded. These studies were performed on multiple mixed monolayers with varying azobenzene-glycolipids in head size to investigate the relevance of the head group. Differences in terms of their switching behaviour and membrane conformations will be discussed.

Physics-Based Impedance Model to Diagnose Pore-level Effects in PEFC Electrodes

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The performance of a polymer electrolyte fuel cell (PEFC) depends to a large extent on the microstructure and properties of porous electrodes. The porous network of the cathode catalyst layer (CCL) is responsible for various transport and kinetic limitations that determine catalyst effectiveness and cell voltage. The typical CCL has a complex porous structure that consists of primary pores with nanoscale dimension that exist inside of primary carbon particles or between carbon particles within particle agglomerates and mesoscale pores between agglomerates. The former type of pores are vital for the effective electrocatalytic activity whereas the latter control the transport of reactant molecules [1]. Hence, diagnosing this structure (under different conditions), is essential to rationalize the interplay of transport and reaction. Electrochemical impedance spectroscopy (EIS) is extensively used as a noninvasive diagnostic tool for material characterization and to investigate the state of health of the PEFC [2,3]. We present a physics-based EIS model to investigate the effect of various morphological features at the pore level on the impedance response. A water-filled Pt nanopore with a single opening is modeled as a segment of a representative element in an electrocatalytically active agglomerate (Fig. 1). The model accounts for double-layer charging, proton conduction and oxygen transport in the pore along with non-monotonic surface charging at catalyst surface.

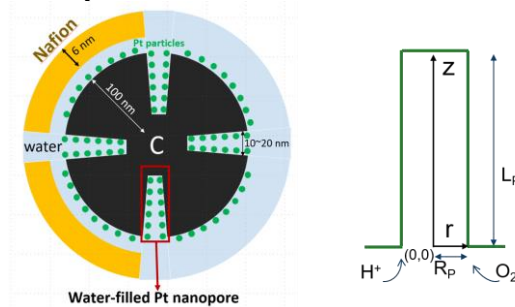


Figure 1: Schematic of the model system showing Pt lined nanopores extending into the agglomerate.

We will present approximate analytical solutions for the impedance response in various limiting cases. Effects of pore dimensions on the reaction penetration depth infers catalytic effectiveness under various operative conditions and hence the sensitivity of impedance response to pore scale structure is investigated. Influence of the interplay between this phenomenological length scale and morphological length scales is analyzed for the obtained solutions. We discuss the capabilities of the model to investigate the fundamental underlying structure-property-performance relationships in PEFCs and extend it to extract electrode structure information from measured impedance data.

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Rational design of catalytic surfaces for fuel cell technologies by selective molecular patterning

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Current green technologies are not ready for mass commercialization, and demand for deep and fundamental research, especially regarding the design of efficient catalytic materials. In this sense, selective molecular patterning can be employed for the development of highly active electrocatalysts[1]. Studies have shown that adsorption of foreign adatoms on Pt can improve its catalytic performance and stability.

Here selective molecular patterning of Pt surfaces with Bi, and Te adatoms has been studied using DFT to explore changes in the electronic properties and provide a deeper insight into the factors governing the adatoms' adsorption process.

Results indicate that both adatoms strongly adsorb on all low-index platinum surfaces, and become positively charged upon adsorption, as expected from the difference in electronegativity between adsorbate and substrate. The work function decrease of Pt is seen upon Bi and Te adsorption [2] and the trend for its decrease changes from(111) > (100) > (110) in clean surfaces [3], to (100) > (110) > (111) in Bi(Te)-Pt surfaces, evidencing differences in the redistribution of the electron density depending on the orientation of the surface. Similarly, adsorption of either Bi or Te also causes a downshift of the d-band center of Pt. Thus, even at low 1/16 ML coverage Bi and Te not only may block active sites on platinum, but also have a more fundamental impact on its catalytic properties.

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Towards Constant Potential Modeling of CO-CO Coupling at Liquid Water-Cu(100) Interfaces

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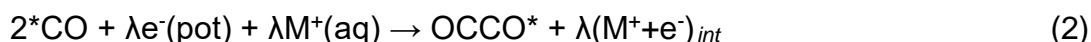
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We use density functional theory, molecular dynamics, and metadynamics to study electrochemical *CO-*CO coupling at water-Cu(100) interfaces in the presence of explicit electrolyte.¹ We consider both the *CO-*CO coupling reaction and the charging process required to keep the potential constant. The charging process consists of transferring explicit cations from the electrolyte ($M^+(aq)$) and electrons from the potentiostat ($e^-(pot)$) to the interface ($(M^+e^-)_{int}$).

Under constant charge conditions (eq 1) (non-constant electrostatic potential), the *CO-*CO coupling reaction energies are relative insensitive to the charge state at the interface and the electrolyte composition (Figure 1b). The *CO-*CO coupling reaction is not spontaneous at any of the constant charge conditions we consider.



Under constant potential conditions (eq 2), the *CO-*CO coupling reaction is stabilized at lower potentials because of charging and the reaction is influenced by the electrolyte composition. The constant potential *CO-*CO coupling reaction changes the electrosorption valency (λ) by around 0.4-0.5 and the process becomes spontaneous below ~ -1.2 V vs. SHE.



Our approach can be used to convert energetics from ab initio molecular dynamics determined at constant charge to estimates at constant potential and is generally applicable to electrochemical processes (or chemical steps involving significant dipole changes).

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Establishment of the Potential of Zero Charge of Metals in Aqueous Solutions: Different Faces of Water Revealed by Ab Initio Molecular Dynamics Simulations

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Understanding the mechanism of PZC establishment at metal/solution interfaces is a lasting focus in electrochemistry. Herein, taking Pt(111)/water and Au(111)/water interfaces as model systems, a series of ab initio molecular dynamics (AIMD) simulations and density functional theory (DFT) calculations have been performed to clear the underlying causes of significant decrease in PZC as metal contacting with aqueous solution.^[1] Through carefully correlating the interfacial atomic and electronic structures, we reveal that the first layer of O-down water molecules (W_{M-O}) significantly lowers the PZC, through pushing spilled electrons back into the metal skeleton and by transferring electrons to metal surface through coordination bonds. The pivotal role of W_{M-O} in regulating the PZC of metal electrodes is further verified by a non-monotonic PZC change upon adding H₂O with varying coverages. In sharp contrast, the water molecules in H-down configuration (W_{M-H}) in the second solvation layer elevate the PZC through chemical interaction and orientation dipole. Moreover, the second solvation layer also contains water molecules without preferred orientation (W_{Free}), which merely participate in the hydrogen bonding network and negligibly interact with metal electrode. These atomic insights not only help to enunciate the long-standing puzzle of a significant decrease in PZC of metal electrodes by solvation, but also add our understanding to the behaviors of metal-solution interfaces, for examples, the potential and adsorbate-dependent interfacial capacitance.

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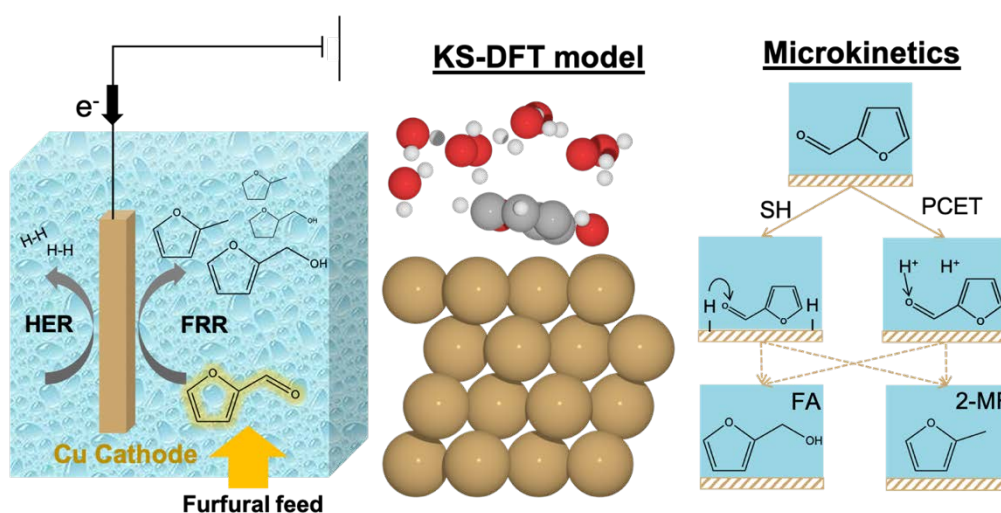
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Theoretical Studies of Furfural Electroreduction on Copper Electrode

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Biomass economy has recently been proposed to serve as potential solution to global crisis concerning both environment and energy¹. Sustainable energy generation could be achieved via electrochemically transforming biomass waste into fuels and value-added chemicals. Furfural, as an important platform biomass derivative, has been used to produce valuable compounds, such as furfuryl alcohol (FA) and 2-methyl furan (2-MF) via electrochemical conversion². However, due to the complexity of these reaction at the electrolyte-electrode interface, the mechanism involved in the conversion to various products and the relationship between hydrogen evolution reaction (HER) and furfural reduction reaction (FRR) remain unclear. Here, we apply ab-initio based kinetics modeling in combination with computational hydrogen electrode (CHE) model to study HER and FRR towards FA and 2-MF on copper at different cathode voltages in acidic conditions. We successfully obtain the simulated polarization curves for HER at acidic pH (0, 0.5 and 3), and the trends in onset potential for H₂ agree with experiments. Moreover, based on the kinetics for surface hydrogenation (SH), we suggest the predominance of proton-coupled electron transfer (PCET) pathways over SH ones during FRR on Cu electrodes.



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Boosting Hydrogen Evolution Reaction by Lateral Electrode Structuring

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Producing solar fuels with devices based on metal-insulator-semiconductor (MIS) interfaces is a very promising future technology for a renewable energy economy. The semiconductor part of such hybrid devices can provide an efficient absorption of solar light while the metal part facilitates fast reaction kinetics. However, in order to fulfil these two functionalities, the device requires patterning of the MIS interface.

We show that lateral structuring of silicon-based electrodes with well-defined gold arrays produced by Lift-off Nanoimprint Lithography exhibits cooperative effects [1], i.e. strongly altered catalytic activities compared to bare metal surfaces or metal particles on conductive supports. We demonstrate this with the Hydrogen Evolution Reaction (HER) in acidic and alkaline medium and show that the HER rate scales with the interfacial area between the metal catalyst and the adjacent silicon oxide support. The rate of alkaline HER can be enhanced by an order of magnitude, which results in a very similar HER activity in alkaline and acidic medium. We explain this increase by a bifunctional mechanism at the metal/silicon oxide interface and argue that the lateral structuring changes locally the electric field, which, in turn, increases the reaction rate of alkaline HER at the interface compared to the rate at the metal bulk. [2]

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Interfacial pK_2 of carbonic acid at the Pt(hkl)/solution interface

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Pt(111) electrodes in contact with 0.1 M perchloric acid solutions saturated with CO₂ show spectroelectrochemical signals associated to adsorbed bicarbonate and carbonate anions [1]. The relative intensities of the absorption peaks at different pH and applied potential can be used to determine the interfacial pK_2 of carbonic acid, which results considerably smaller than in solution phase, irrespectively of the assumptions made in the analysis of data [1-3]. The study on the Pt(111) electrode benefits from the fact that CO₂ is not reduced to adsorbed CO on this surface, thus enabling to determine the necessary coefficients related to the adsorbed carbonate and bicarbonate species through a simple interfacial mass balance which involves the consumption of dissolved CO₂.

On other Pt(hkl) structures, the reduction of CO₂ to CO will disturb this mass balance and complicate the band analysis and the subsequent calculation of the corresponding surface pK_s . However, it is still possible to gain this information under appropriate experimental conditions, i.e. adjusting the lower potential limit to avoid the reduction to CO by adsorbed hydrogen. In addition, assuming that the absorption coefficients are those determined for Pt(111), the corresponding surface pK_s can be estimated.

In this study the stepped surfaces vicinal to the Pt(111) pole have been examined. For the Pt(110), the surface pK_2 is lower than that of Pt(111) at the corresponding potentials of zero free charge. This means that the more open surface behaves as being more alkaline than the closest packed one and thus adsorbed bicarbonate dissociates more easily to adsorbed carbonate

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Electroosmotic Flow Grows with Electrostatic Coupling in Confining Charged Dielectric Surfaces

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In this work [1], the effects of polarization of confining charged planar dielectric surfaces on induced electroosmotic flow are investigated. To this end, we use dissipative particle dynamics to model solvent and ionic particles together with a modified Ewald sum method to model electrostatic interactions and surfaces polarization [2]. A relevant difference between counterions number density profiles, velocity profiles, and volumetric flow rates obtained with and without [3] surface polarization for moderate and high electrostatic coupling parameters is observed. For low coupling parameters, the effect is negligible. An increase of almost 500% in volumetric flow rate for moderate/high electrostatic coupling and surface separation is found when polarizable surfaces are considered. The most important result is that the increase in electrostatic coupling substantially increases the electroosmotic flow in all studied range of separations when the dielectric constant of electrolytes is much higher than the dielectric constant of confining walls. For the higher separation simulated, an increase of around 340% in volumetric flow rate when the electrostatic coupling is increased by a factor of two orders of magnitude is obtained..

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Building a theoretical prototype of a Hodgkin-Huxley neuron using 2D nanofluidic memristors

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New energy-efficient architectures inspired by the mammalian brain have been growing as an alternative to traditional von Neumann computing. Yet, existing hardware implementations use electrons as charge carriers, while neurons rely on transport of ions for both computation and the building of memory. Because ions come with own “flavor” – their mass, size, chemical structure, etc. – they make biological intrinsically more versatile. In my poster, I will focus on a recently demonstrated device, consisting of a single molecular layer of water and ions confined between atomically smooth surfaces. I will show that these experimentally available systems can exhibit exotic ion transport properties, leading to neuromorphic behavior. I will show that ions in such two-dimensional electrolytes form tightly bound Bjerrum pairs, that assemble into micelle-like clusters upon application of an electric field. The long-timescale dynamics of these ionic assemblies are at the source of memory effects in the system's conductivity – a behavior known as “memristor effect”. Guided by analytical predictions, I will also present molecular dynamics simulations of nanofluidic circuitry incorporating coupled memristor building blocks. The resulting system is capable of spontaneously emitting voltage spike trains, in accordance with the Hodgkin-Huxley neuron model. These findings reveal a minimal, experimentally-accessible biomimetic neuron architecture based on nanofluidic channels, paving the way for the development of ion-based computing and prototype ionic machines.

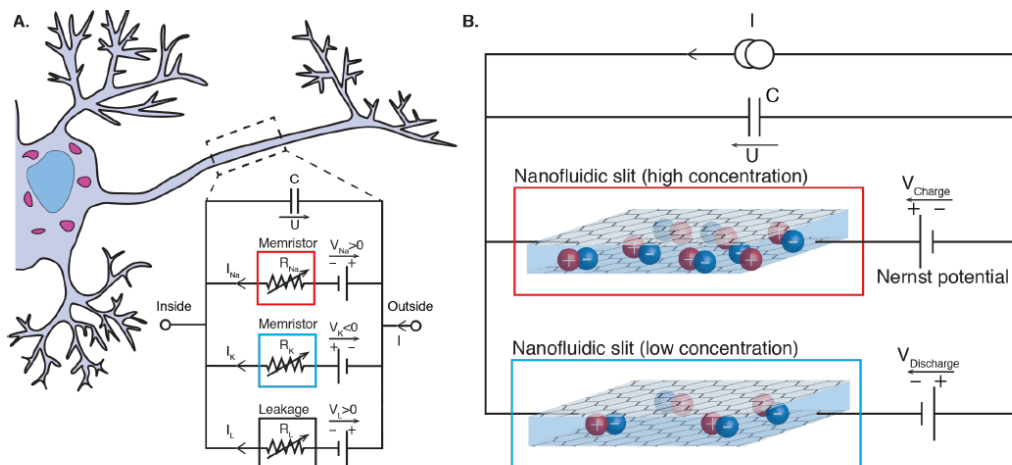


Figure – The Hodgkin-Huxley neuron model (A) and its nanofluidic equivalent (B).

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Magneto-optical probing of magnetic-field facilitated electrochemical hydrogen evolution enhancement

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The structure and dynamics of electrode-electrolyte interfaces are fundamental to decreasing the overpotential and improving efficiency of water splitting reaction. Of particular interest are processes that happen on a nanoscale under applied magnetic fields, as it was demonstrated that the latter can be used to enhance the efficiency of the process. However, the overall impact of magnetic field on electrochemistry is poorly understood. One of the challenges lies in the incompatibility of the analytical requirements (e.g. bulk aqueous and extreme pH environment) with the available interface-sensitive techniques (e.g. XPS). Here, we present an electrochemical magneto-optical set-up that overcomes such challenges and allows probing an electrode in an applied magnetic field, while simultaneously monitoring current densities under reaction conditions.

We report a 7% increase in the electrochemical current density with Pt hydrogen evolution electrode in 0.1 M KOH under moderate applied bias (-0.15 V (vs RHE)) and magnetic field (250 mT). Within the defined parameters, the electrode remains structurally and chemically stable, and the effect is assigned to the nanoscale-facilitated changes within the electrochemical double layer.

Computation of Solvent Effects in Electrochemical and Organic Systems

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The effects of liquid solvents on structural, electrochemical and thermodynamic parameters of surfaces and molecules are of utmost importance for understanding phenomena at electrochemical interfaces and in organic liquids. However, solvent modeling represents a great challenge to theory and computation. We will discuss state-of-the-art approaches that we utilise for scrutinizing liquid-phase driven phenomena. In the case of electrochemical interfaces, the main challenge is the lack of a self-consistent treatment of the solid/liquid boundary [1,2]. In this regard, we intensively tested the Effective Screening Medium Reference Interaction Site Method (ESM-RISM) [3] that combines Density Functional Theory (DFT) with the integral theory of liquids. We will discuss promising results that we obtained with this method for the description of Pt(111)/electrolyte interfaces at different electrode potentials. Another challenge, common to electrochemistry and organic or biochemistry, is the computation of thermodynamic parameters of liquid phases, either electrolytes or organic solutions. In that respect, we will discuss our successful application of recently developed computational schemes (ESM-RISM and SCCS methods [3,4]) and theoretical models [5] for an estimation of the entropy of liquid phases. These allowed, for instance, for understanding of radiolytic degradation mechanisms of liquid organic extractant agents in dodecane solution and are currently applied to understand the variation of electrolyte entropy at electrochemical interfaces.

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Ab-initio electrochemical kinetics simulation methodology coupled to continuum models for describing trends in the oxygen reduction reaction

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A major challenge preventing complete understanding of reactions at the metal | solution interface is determining ab-initio barriers at constant driving force under realistic conditions. Current state of the art methods are computationally expensive, requiring calculations to be done at different unit cell sizes and with explicit treatment of the electrolyte. In this work, we develop an approach to simulate the electrode-electrolyte environment at minimal computational expense. These ab-initio calculations serve as inputs to parameterize a continuum model of the electrochemical interface. We apply this methodology to explain trends for differing cation identity in the oxygen reduction reaction (ORR) and more generally to peak positions in cyclic-voltammograms. We show that pH dependent experimental trends within the ORR are captured on the basis of this model.

Modelling of Lithium Droplet Formation During Lithium Dissolution

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Lithium metal anode batteries have regained a lot of research attention as they are promising candidates for next-generation energy storage systems. However, the poor Coulombic efficiency limits the battery's cyclability. The main causes for low efficiencies are the irreversible loss of active lithium due to the formation of a solid electrolyte interface (SEI) and the formation of unreactive "dead" metallic lithium which is disconnected from the current collector [1]. Experiments show that during the dissolution of lithium whiskers, which grow as irregular structures during plating, the tip cannot be dissolved [2]. We developed a generalized phase-field model of the dissolution process to gain insights into the underlying mechanisms of "dead" lithium formation and capacity fade.

Our model describes the dissolution of a single lithium whisker in a liquid electrolyte based on lithium surface tension and the interaction between lithium and the interphase, utilizing the framework of non-equilibrium thermodynamics [3]. We study under which circumstances instabilities occur and dead lithium forms. Our model predicts the nucleation of an instability for low stripping current densities, induced by interactions with the SEI. This leads to an incomplete dissolution and the formation of an electrically disconnected metallic lithium droplet, in agreement with optical microscope observations of lithium dissolution [2].

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Title: Carbon Nanotube Porins: Bio-Compatible Nanofluidic Circuitry

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Abstract:

Nanofluidic channels confine water and ions down to the length scales that are comparable to the sizes of individual molecules. This strong confinement creates unique phenomena, such as unusual selectivity patterns and strong electroosmotic coupling. To probe the transport behavior and underlying physics under extreme confinement, our group developed a model system - carbon nanotube porins (CNTPs), which are analogs of aquaporins made of carbon nanotubes. CNTPs have well-defined diameters that range from 0.6 to 1.5 nm and ultrashort lengths of ca. 10 nm. CNTPs also have the ability to self-insert into lipid bilayers and live cell membranes, forming artificial membrane channels. We have demonstrated strong cation selectivity in 0.8 nm diameter CNTPs. Further studies showed that built-in charges, environmental changes (such as altering pH), or external forces (such as applying a gate voltage) could alter the ionic distribution and selectivity of these channels, which resulted in ionic current rectification and diode-like or transistor-like behaviors. Our CNTPs represent a versatile nanofluidic model system that we can utilize to advance our understanding and control of ion and water behavior at nanoscale, which could further benefit lab-on-a-chip sensing or drug delivery.

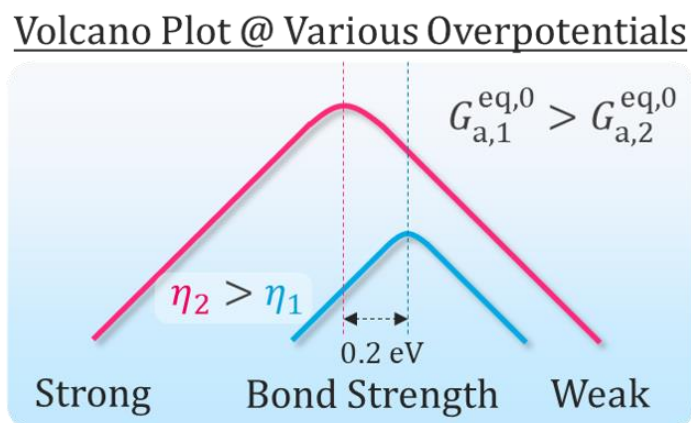
Criterion for Finding the Optimal Electrocatalyst at Any Overpotential

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The volcano plot is widely employed to compare the activity of different electrocatalysts using a small number of descriptors. It was recently demonstrated that the apex of the volcano curve shifts with applied potential. However, the trend of the potential-dependent shift of the volcano apex has remained unclear. Herein, we address this question by a generic two-step electrocatalytic reaction. With the transfer coefficient assumed as 1/2, the presented analysis reveals that the adsorbate coverage at the volcano apex equals 1/2 regardless of potential. A criterion is derived that predicts the shift of the volcano apex in terms of the activation energies for the two steps. This criterion is further generalized and applied to the oxygen reduction reaction. Following that, the influence of the transfer coefficient and the potential of zero charge on the volcano plot is revealed. Implications of the presented criterion for targeted design of electrocatalysts are discussed.



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Phase Separation of Polyelectrolytes: The Effect of Charge Regulation

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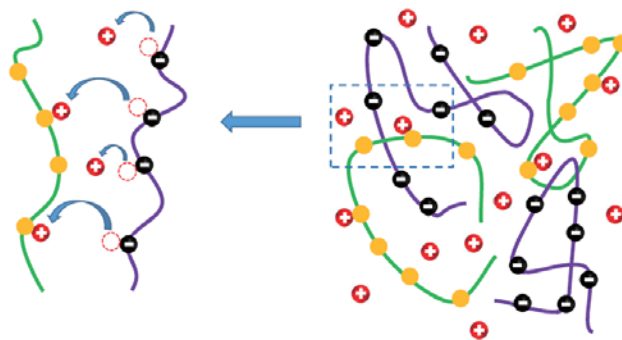
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Complex coacervation, known as the liquid-liquid phase separation of solutions with oppositely charged polyelectrolytes, has attracted substantial interest in recent years. We study the effect of charge regulation (CR) mechanism on the complex coacervation, by including short-range interactions between the charged sites on the polymer chains, as well as an association-dissociation energy parameter in the CR mechanism. We investigate the phase diagrams of two CR models: (i) the hopping CR model (HCR); and, (ii) the asymmetric CR model (ACR). It is shown that during the phase separation, the polymers in the condensed phase are more charged than in the dilute phase, in accord with the Le Chatelier's principle. In addition, "secondary CR" effects also influence the change in the volume fraction of the two phases. The latter can cause the charge difference between the two phases to change non-monotonically as a function of the CR parameters. These predictions are subject to future experimental verifications.

Phase Separation:
Self-Interaction & Charge Regulation



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Origins of potential dependent Tafel slope of electrochemical CO₂ reduction on silver

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The electrochemical reduction reaction of CO₂ (CO₂RR) to fuels and chemicals is an appealing pathway to store intermittent energy and to alleviate global warming at the same time. Understanding the reaction mechanism of CO₂RR to CO is an important step to optimize the catalysts for CO₂RR. Despite extensive research on this reaction, controversy still exists on the reaction mechanism, especially on the Tafel slope. Here, we develop a multiscale model for CO₂RR on Ag electrode, which unifies the microkinetics, the surface charge effects and the mass transport phenomena into a coherent picture. The model explicitly captures the experimental CO polarization curve and reveals the anomalous decreasing CO current density at high overpotentials is mainly caused by lateral interactions. Besides, we show the experimentally observed Tafel slope ~59 mV/dec at low overpotentials is the combined result of intrinsic slope ~39 mV/dec and surface charge effects, the increasing Tafel slope at medium overpotentials is the combined result of intrinsic slope ~118 mV/dec, surface charge effects and mass transport limitations.