Fundamental Electrocatalysis: Theory Meets Experiments - Leiden, from 26 Jun 2017 through 30 Jun 2017

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Charge transfer reactions in electrochemical environment underpin the operation of emerging energy and information technologies. Understanding these processes at the atomistic level is a key for their optimal design.

In our workshop we have considered the **main open challenges in electrocatalysis**, namely: 1. disclosing the functional relationship between double layer, potential drop at electrified interfaces and the effect of an applied potential to a cell. 2. Developing new comprehensive models for electrocatalysis at novel, efficient and non-precious catalysts. 3. Gaining insight into the origin and control of forces, charge transfer, atomic dynamics and reactivity at the nanoscale.

We reviewed the multifaceted phenomenon of electrocatalysis at the nanoscale from theoretical, computational and experimental perspectives, from fundamentals of electron transfer to commercial applications. We focused on developing a truly multidisciplinary perspective, which is critical to successfully close the gap between theory, experimental insight and technological applications.

The **outstanding level of our speakers and the oral presentations**, the common willingness to push forward the traditional communities' boundaries expressed in our participants' invaluable comments and suggestions during the discussions turned this workshop into a **remarkably vibrant scientific event**.

The modern challenges of electrocatalysis were discussed from different perspectives and are briefly summarised in the following paragraphs.

The most important strategies and quantities to be modelled in modern electrochemistry were analysed in depth. The need for going beyond the standard hydrogen electrode computational scheme emerged in many occasions, developing more refined models for solvation (Gross, Dabo, Reuter), overcoming the assumption of proton-coupled electron charge transfer and performing kinetics studies. How to model the effect of the applied potential and charge polarization at interfaces was discussed in depth (Schmickler, Gross, Sprik, Chen), as well as the issue of energy-level alignments (Reuter, Thygesen) and the relevance of surface science studies on semiconductors to understand electrochemical processes (Todorova). The effectivity of adopting *in-depth* approaches aiming at representing realistically the electrochemical environment was compared to computational screening approaches to span a broad range of materials using traditional descriptors (Skulason), possibly aided by robust screening methods (Gavartin). Theoretical and experimental studies on cheaper and more efficient catalysts for molecular (O, CO_2, N_2 and more) oxidation and reduction reactions were proposed, connecting model surfaces to nanostructured systems (Chan, Skulason, Bandarenka).

All the different communities agreed about the need for a better resolved experimental observation of fundamental electrocatalytic processes in electrochemical environments. The great potential of nano-spectroscopies and microscopies (and, in general, of combined experimental investigation) was clearly highlighted, in view of the understanding of structures and energy conversion processes at interfaces (Domke, Roke, Backus, Tromp, Kunze-Liebhäuser). Remarkable examples were presented controlling charge and structure of electrified interfaces and transformations therein (Rupp, Schmidt, van Ruitenbeek) and its effect on the electrocatalytic activity.

Intense debates in the specific discussion groups led to a new perspective on electrocatalysis. For example, important similarities and differences between charge transport phenomena in molecular electronics and electrocatalysis were discussed, found in the common experimental setup – which includes an electron source, a gate, an electron drain and a solvent. To the best of our knowledge, such non-conventional perspective on the electrocatalytic phenomena had not been discussed before (Seideman, Di Ventra, Thygesen, Chiechi, Rudolf).

The ideas and concepts generated during our workshop are evolving into a **review paper**, to be submitted to Chemical Society Reviews of the Royal Society, and further to the formation of a new larger interdisciplinary community, through a H2020 **COST action**.

Our workshop lasted 5 days. We had 60 participants, 25 of whom were invited speakers. Our workshop was **distinct from a regular conference both in terms of structure and purpose**. (a) We asked all the speakers to introduce the whole audience to their own field of study and to highlight the challenges they are facing. (b) There were no questions and answers at the end of each talk – the discussion of each two or three talks was grouped into a single discussion session, to keep the discussion multidisciplinary. (c) A scientific questionnaire was distributed well in advance of the conference where participants were asked to provide their personal input, views and ideas, reflecting on the three main challenges proposed by this workshop and to reflect on the links between the different communities present. A copy of the questionnaire is attached below. (d) The central part of this workshop was devoted to thematic group discussions, where each participant could speak out and discuss the issues raised in the questionnaires. At the end of each group a written report – attached below - was delivered to the organisers. We had two group sessions and five groups per session. Every group had a coordinator and two co-coordinators. Participants were asked to enroll into a group of their choice. The identity of coordinator and co-coordinators was decided by the organisers for the first session in order to enforce a multidisciplinary discussion within each group. An expert of the theme of the group and two scientists with complementary expertise were included in each group. The group coordinators of the first session were: Group 1: Sprik /Van Ruitenbeek / Santos; Group 2: Gross / Rupp / Thygesen; Group 3: Shmickler / Backus /Kunze-Liebhäuser; Group 4: Honkala / Schmidt / Chan; Group 5: Di Ventra/Filhol/ Todorova. In the second session every group elected their coordinators. (e) To further favor the discussion among participants, we limited the frontal lectures to a maximum of three hours per day and included several coffee breaks. The late afternoon and evening of day 3 was dedicated to the conference dinner and boat trip.

We think that the special format adopted was particularly fecund. Especially the idea of having an arched discussion session each two/three oral presentations nailed our purposes, promoting multidisciplinary and general discussions, yet, on the specific session topic. The small group discussions stimulated an open and dynamic exchange of ideas. Overall the workshop was very intense in terms of time and topics discussed therein, yet its **thoroughly planned schedule and structure** allowed swift communication among the different communities. The success of the workshop was also due to the exceptionally high quality of the invited speakers, the day chairs and discussion leaders, who always had the ability to find bridges between the different ideas discussed.

Two plenary discussions were organised at the beginning and at the fourth day of the workshop. Young scientists were specifically invited to present their perspective. All off them and also many senior participants explicitly claimed that the workshop provided a very educational and stimulating experience. A flash poster presentation and poster prize (€200 to the winner and €100 for second and third places) was set up to favour active participation of young scientists. The first prize was assigned to Bohdan Yeroshenko Debye Institute, Utrecht University (NL); second and third prizes to Nicholas Hoermann, THEOS, EPFL (CH) and Lisa Dreier, MPI Mainz (DE).

Finally, we are proud that about 50% of the speakers and the large majority of chairpersons were both young and senior women. This is quite exceptional for any STEM event. A special session on gender bias in science was organised during the evening of day 4. The discussion was very animated and stimulating and brought out some of the hidden biases against women still present in the STEM society.

We are grateful to Lorentz Center for hosting our workshop with generous financial and organizational support. We thank Psi-k Network and Schroedinger company for generously sponsoring our workshop.

The organisers:

Konstantinos Antonopoulos (Munich, Germany)

Federico Calle-Vallejo (Leiden, The Netherlands)

Clotilde Cucinotta (Dublin, Ireland)

Marc Koper (Leiden, The Netherlands)

Monica Kosa (Haifa, Israel)

Questionnaire

What are the biggest challenges for developing effective models (experiments) for the description of electrochemical environment and charge transport / chemical transformation therein - under applied potential and flowing currents - that is both realistic and computationally (experimentally) viable? What is your view/opinion about the three open challenges proposed in our workshop? Why it is important to address the open issues you propose? What are the main open questions emerging from your research/field? What are the limits and assumptions of current approximations/models? How do you think these limits will be addressed in future? How can we progress towards a more realistic description of EC environment?
What theoretically (experimentally) relevant information should we extract from experiments (theory) in order to capture the complexity of multiscale, non-equilibrium EC phenomenon? How can experiments (theory) help theory (experiments) to help you answering the open questions in your field?
What would you ask to the Molecular Electronics (Electrochemistry) community to help you answering the fundamental open questions in your field? What are the common questions around the themes of our workshop for Molecular Electronics and Computational Electrochemistry? Are there any promising common research patterns for Fundamental Electrocatalysis and Charge Transport?
What else would you like to discuss during this workshop?

Working groups -

Group 1 - L*ocal vs. macroscopic electrode potential*. How to compute, analyse and control the potential across the double layer? A*pplied potential*, *periodic boundary conditions and dielectric response at electrified interfaces*.

Session I - Tuesday, 27 June 2017 11:00 – 12:30

Different approaches to describe the electrochemical interface:

From atomistic level or using, for example, continuous models (dielectric constant).

Can be obtained reasonable capacitance values for the DL from continuous models? Yes, sometimes, but does it mean a “good” description?

How can be described in a realistic way the presence of ions and their solvation?

How large are the screening effects?

What is “adsorption”?

Relationship between work-function and pzc:

How it affect the adsorption of species, the presence of the solvent, the evaluation of the work-function and the pzc? (electronic charge redistribution). Electrosorption valence?

Thermodynamics --- Kinetics. To describe reactivity: not only thermodynamics is important, Kinetics must be addressed.

Description of HOMO – LUMO differences is not sufficient good by DFT.

Group 2 - Comprehensive description of electrified interface and charge transfer reactions therein. Bridging different timescales; progressing from thermodynamics to kinetics studies; Correct level alignment and charge transfer.

Session I - Tuesday, 27 June 2017 11:00 – 12:30

Challenge: comprehensive description of electrified interface and charge transfer reactions therein.

The view on challenges strongly depends on the background

Goal: Find smart ways to include electrochemical environment

In principle we know how to describe the presence of an aqueous electrolyte: Large explicit system plus thermodynamic integration schemes

Electrode potential: In principle it requires a grand-canonical scheme for the electrons (Mermin theorem in DFT) which can be realized by varying the Fermi energy. Problem with periodic setups: they require keeping the periodic cells charge-neutral. Where do we put the countercharge when we change the number of electrons?

Session II - Wednesday, 28 June 2017 14:00 – 15:00

Experiments on molecular conduction under electrochemical conditions, i.e. varying electrode potential: How instructive will this be for electrochemistry?

Difference between the electrochemical potential (work potential) and inner potential (f). Is computing work functions, electrochemical potentials all there is to computational electrochemistry?

Is the capacitance a fundamental quantity? Can it be computed by comparing electrochemical potentials?

Group 3 - Characterization, reaction intermediates, surface structure, defects, coverage, binding energy, charge, potential drop at the EI and the effect of the applied potential on these quantities.

Session I - Tuesday, 27 June 2017 11:00 – 12:30

Combine different methods to get macroscopic and molecular level information; e.g. STM to get current and molecular level picture

Go back to well-defined methods from 70ths-80ths; many systems very well characterized by then; we might forget them and try to develop everything again

Use Hg-electrodes as they renew itself and are thus highly precise; however, as they renew, one cannot see them in the real catalytic state

Hydrogen evolution is the most studied system, but the least understood

Discussion about timescales in experiments and simulations. In experiments one can address easily ms to s timescale; laser spectroscopies useful for fs to ns timescale. There is a gap in between. Microseconds might be possible with imaging techniques to fill the gap at least partly. Of course, theory is only possible on short timescales. One way to combine timescales in experiments and theory might be heat jump experiments.

Discussion about effect of ions on catalytic efficiency; we discussed about ions that are in principal spectators in the reactions, e.g. cation in reaction with negatively charged surface. By changing the ions one might change as well the level of impurity. It would be great if we can develop a method to look at the ion influence on surface reactions. What happens in the first few water layers? One way to address these issues from theoretical point of view could be to perform first a simulation with DFT, e.g. OH on surface to calculate the charge. Then classical MD as that can handle charge; one could then see if and how the cations come to the surface.

Regarding oxygen evolution; compare activity trends between experiments and theory in order to obtain molecular level detail. Probing the OH intermediate. Again combination of different methods needed to get a clear molecular picture.

Sometimes samples are cooled down to see intermediates, e.g, only way to see CO intermediate on Cu in CO_2 reaction. However, one has to realize that then as well the reaction pathway might be influenced; different reaction energies.

Session II - Wednesday, 28 June 2017 14:00 – 15:00

What is the greatest problem in electrocatalysis? Of course, it is not feasible to answer this question definitely within a brief discussion session - and even barring time constraints, opinions may vary. Still, it is possible to list the most important conditions an electrocatalyst must fulfill:

- Selectivity and reducing or preventing unwanted side products;
- High turnover rates towards the desired product;
- Stability and sufficient lifetime in operating (electrochemical) environments;
- Affordability and availability of catalyst materials.

One thing we could agree upon is that these problems are associated with optimization problems, which we need to solve for each target process.

For increasing the turnover rate for great scale diffusion limited processes, increasing the surface area may be best, even up to making (potential) tunable microporous reactors and catalysts. However, for reactions requiring greater selectivity (or which are more potential sensitive) one must focus on the surface science details.

Currently, most (if not all) permutations of properties and solvents are modelled separately by hand. This effectively limits the number of alternative models, system compositions and configurations we can research within any project, leading to less well-supported reaction models and missed opportunities for further catalyst improvement. Moreover, (current) DFT models generally are bad at predicting quantitatively accurate properties, and good at finding reactivity trends. Hence, we should not try to struggle our way towards quantitatively correct theoretical methods straight away, but instead upscale our theoretical calculations to span a broad range of parameters or alternatives aided by machine learning methods.

But what about the experimental aspects of electrocatalysis? In order to learn more about catalytic pathways and intermediate properties, we should think beyond IV curves and traditional spectroscopy. By combining analytic techniques and knowledge from various different fields with the state of the art in electrocatalysis, we can further both our experimental knowledge and use that knowledge to improve our electrochemical models, which itself provides new leads towards more targeted experiments.

Altogether, we must combine large-scale smart (machine learning supported) computational assays and broad ranges of (combined) analytical techniques to further both theory and practice while helping them to bring each other to fruition.

Group 4 Electrocatalytic applications, SEI, understanding electrochemical interfaces beyond Pt

Session I - Tuesday, 27 June 2017 11:00 – 12:30

Developing new comprehensive models and applications for electrocatalysis at novel, efficient, and also non-precious catalysts

Viable technologies

- Shell:
    - Requirement: big, cheap – sizable compared to global energy system
    - Renewable energy will become cheap – electrochemistry at forefront
- BMW:
    - Need cheap materials
    - Mandatory to go beyond Pt for fuel cells? – good to try out products
    - Pt is also used for car exhaust?
    - Can Pt just be utilized better?
- Cu to produce ethylene?
    - Ethylene from oil cracking
    - Need to compare to current prices of the product, overpotentials too high
    - Durability, technoeconomic analysis?
- Ethical to get materials?
    - Everything that is mined comes with political problems
- Decentralized production through electrochemistry?
    - e.g. methanol - capture CO_2 & concentration – a challenge - then do it?
    - Make your own H_2?
    - Economy of numbers vs. economy of scale – need to do the analysis
- Possibility of 2 parts synthesis – syngas from electrochemistry then for instance FT to make hydrocarbons

Beyond simple models – beyond descriptor based models?

- Correlations based on relation mapped out by theory, based on fundamental understanding
- Cause-effect relationships, need fundamental understanding
- Sequentially add complexity
- Scaling as a good way to predict catalyst, when they are well defined
- Deal with complexity by finding new descriptors
- Agreement with experiment: trends, within 2 orders of magnitude agreement with experiment already very good based on current models
    - Need to do research that is relevant for society, lead to a product
    - Upscaling – other problems – relying on trends probably sufficient
- Role of theory to help understand trends in experiment – are trends enough?
- Role of science to think about what is relevant, help industry with designing a plant
- Need for more discussion between industry and scientists
- Predictive descriptors are needed – not just rationalization of existing results

- For computational screening – binding energy is not very satisfactory – we need to improve understanding of binding energies, or improve brute force methods – neural network potentials

Activation energies and pre-exponential factors from T-dependent experiments

- Arrhenius plot is flawed? How to interpret it?
    - Activation energy and pre-exponential factor goes down
    - Classical problem beyond electrochemistry
    - Why they change with potential e.g. Wolfgang’s
- Deconvolute transport phenomena from activation energies?
- Need for more data

Electrodeposition phenomena

- How do materials change during reaction
- Restructuring
- Surfactant-induced reconstructions from Nuria Lopez
- Look for descriptor-based approaches?
- Very sensitive to impurities

Experimentally characterize the active sites

- EC-STM – does it reflect behavior of defects?
- Graphite/basal plane HOPG? Start introducing defects
- In situ XAS monitor oxidation state?
- Probably not static
- Series of stepped single crystals, increase step density and measure CO oxidation
- Defects most active so should we be modelling stepped surfaces?
- Many reactants have a roughening effect; descriptor for this?

Explicit solvent modelling at given temperature and pH

- Hybrid approaches?
- Benchmarking to explicit methods necessary
- Aprotic solvents – but experimentally difficult to deal with

Group 5 - Fundamental charge transfer at interfaces; currents and potential effects on molecular transformation at the nanoscale; towards grand-canonical time-dependent approaches? Going beyond current theoretical frameworks/ approximations?

Session I - Tuesday, 27 June 2017 11:00 – 12:30

Q: Similarities and differences between Molecular electronics (ME) and Electrochemistry

- Experimental setup: Source/Gate/Drain
- Solvent in both systems

e^- transport/e^- transfer

@ the fundamental level: an e^- born in one entity moves through a second entity to reach a third entity

ME: e^- transport from a system with a discrete set of levels to another system with a discrete set of levels via a system with discrete levels

EC: e^- transport from a system with a continuum set of levels to another system with a continuum set of levels via a system with discrete levels

Q: Time scales and time resolution

- How long does an e^- reside on a molecule? Is a reorganization of the molecule possible?
- Can we control/resolve the time scales relevant for the processes of interest?
- Thermodynamics & kinetics
- **In some reaction steps e^- transfer is important, in others not.** Can this be probed/resolved?

Discussion about pH, electrode potential, changes at the interface

→ Need more observables

- local noise spectroscopy possible?

- combining spectroscopy with current measurement

Q: Spin and magnetism:

- need to be careful about what is meant (bulk magnetism, spin on solvated species…)

- can we utilize that H^+ has a spin, while H does not in measurements?

Q: Is it possible to use Greens function techniques in electrochemistry?

The objective drives the method

Observables measured in experiment are inherently averaged quantities.

Session II - Wednesday, 28 June 2017 14:00 – 15:00

What are the similarities and differences between charge transport in the molecular electronics and electrocatalysis?

We concluded that the main difference between the charge transport in these two fields is that in molecular electronics the charge is transferred between 2 continuous states or two discrete states, whereas in electrocatalysis the charge (electron) moves from state to state finally reaching the molecule.

We concluded that good collaboration between the experimentalists and theoreticians is crucial as well as collaborations between both fields since there is a transferable knowledge that can be applied.

Other very important question from the experimentalist working on charge transport in molecular electronics and that no conclusion was reached were:

1. "How does molecular orbitals of self-assembled molecules mix with the metals?" this being an important information to tune the material properties.
2. Where does the potential drop? It seems to be very difficult to determine for this type of systems (molecular junctions).