4th International Conference on **Electrochemistry**

June 11-12, 2018 | Rome, Italy

Keynote Forum

Day 1

Ralph Gilles, Biosens J 2018, Volume 7
DOI: 10.4172/2090-4967-C1-001

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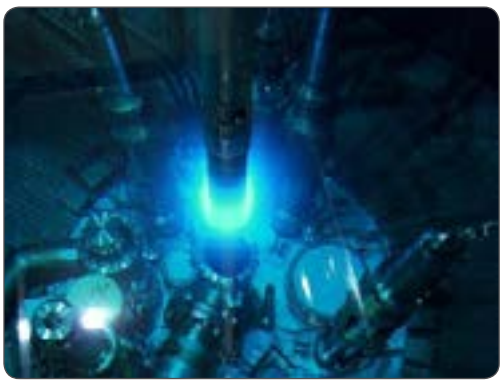
How neutrons as a probe for *in situ* and *in operando* measurements support the understanding of electrochemistry in Li-ion battery research

For a better understanding of the electrochemistry in batteries a huge demand emerge for *in situ* and *in operando* characterization methods. Due to the high penetration depth and high sensitivity of neutrons to light elements as lithium such a probe is more and more attractive in the last decade. This contribution gives an overview how neutrons with their unique properties contribute in the development of new battery cells. During charging and discharging of NMC/graphite cells the intercalation of Li in the graphite layers can be observed *in situ* with neutron diffraction (ND) as such measurements are sensitive to detect LiCx phases as LiC_6 and $LiC1_2$ during the intercalation/de-intercalation process. Under fast charging conditions and low temperatures the appearance of Li plating can be studied. A correlation of C-rates and Li plating is investigated by means of voltage relaxation and *in situ* ND. Batteries consisting of lithium iron phosphate (LFP) are often used for stationary energy storage systems. Here neutrons provide the answer why various types of graphite result in losses of the storage capacity. On larger scales of >50 micrometer neutron imaging (radiography and tomography) enables a non-destructive view inside the cell to make visible for example how the electrolyte filling with the distribution of the electrolyte in the cell between the layer stacks in a pouch cell takes place. The use of neutron induced prompt gamma activation analysis (PGAA) is a powerful tool to describe the capacity loss of the cell caused by tiny metal deposition on the graphite anode after charging/discharging processes. The method of neutron depth profiling (NDP) is suited to study near surface phenomena as the Li distribution in electrodes. A new set-up for NDP is currently under development to improve the space resolution and to measure with a time resolved mode.



Recent Publications

1. Zinth V, V Lüders C, Hofmann M, Hattendorf J, Buchberger I, Erhard S V, Rebelo Kornmeier J, Jossen A and Gilles R (2014) Lithium plating in lithium-ion batteries at sub-ambient temperatures investigated by *in situ* neutron diffraction. Journal of Power Sources 271:152-159.
2. V Lüders C, Zinth V, Erhard S V, Osswald P J, Hofmann M, Gilles R and Jossen A (2017) Lithium plating in lithium-ion batteries investigated by voltage relaxation and *in situ* neutron diffraction. Journal of Power Sources 342:17-23.

3. Paul N, Wandt J, Seidlmayer S, Schebesta S, Mühlbauer M J, Dolotko O, Gasteiger H A and Gilles R (2017) Aging behavior in $LiFePO_4$/C 18650-type cells studied by *in situ* neutron diffraction. Journal of Power Sources 345:85-96.
4. Knoche T, Zinth V, Schulz M, Schnell J, Gilles R and Reinhart G (2017) *In situ* visualization of the electrolyte solvent filling process by neutron radiography. Journal of Power Sources 331:267-276.
5. Buchberger I, Seidlmayer S, Pokharel A, Piana M, Hattendorff J, Kudejova P, Gilles R and Gasteiger H A (2015) Aging analysis of graphite/LiNi1/3Mn1/3O2 cells using XRD, PGAA, and AC impedance. Journal of the Electrochemical Society 162(14):A2737-2746.

Biography

Ralph Gilles a Senior Scientist has his expertise in neutron scattering methods for studying energy materials as batteries and high-temperature alloys. Especially, the use of *in situ*, *in operando* methods (very often combined with non-destructive measurements) on real bulk samples enables a powerful tool on energy related topics. In his group methods as neutron diffraction, small-angle neutron scattering, grazing incidence small-angle neutron scattering, imaging, neutron depth profiling and neutron induced prompt gamma activation analysis are applied for battery research. He is an Industrial Coordinator of Heinz Maier-Leibnitz Zentrum, Coordinator of the Materials Science group and Head of the Materials Science Laboratory.

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Notes:

W Knoll, Biosens J 2018, Volume 7
DOI: 10.4172/2090-4967-C1-001

W Knoll

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Polyelectrolyte multilayer assemblies and brushes on reduced graphene oxide field-effect transistors for sensing applications

Graphene, a two-dimensional zero band gap semiconducting material, has gained considerable interest in material science, energy storage and sensor technology, due to its remarkable electronic and mechanical properties. It's high carrier mobility and ambipolar field effect, together with a great sensitivity towards changes in environmental conditions makes graphene perfectly suitable as transducing material for the use in various types of sensors. In this report, we first describe a novel biosensor exploiting the pH dependence of liquid gated graphene-based field-effect transistors for the enzymatic detection of urea. The channel between the interdigitated source-drain microelectrodes was non-covalently functionalized with bilayers of poly (ethylene imine) and urease using the layer-by-layer approach, providing a LoD below 1 µM urea. Next, we present a sensor based on a reduced graphene oxide field effect transistor (rGO-FET) functionalized with the cascading enzymes arginase and urease as recognition elements in a layer by layer assembly with poly (ethylene imine). The build-up of this nano-architecture was monitored by surface plasmon resonance spectroscopy. L-arginine was quantitatively detected by the change in current between source and drain electrode due to electrostatic gating effects conferred by the formation of OH^- ions upon enzymatic hydrolysis of the analyte L-arginine. And finally, we will describe first results on the coupling of calcium-responsive polymer brushes to graphene field-effect transistors. The presence of Ca^{+2} ions neutralize the charge of the phosphate groups leading to a change of the Dirac point by electrostatic gating effects. A formalism using the Langmuir adsorption model and the Grahame equation is used to obtain the surface coverage from the change of the Dirac point.

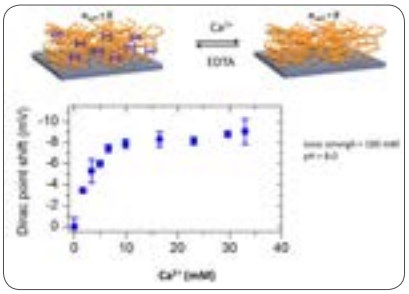

Figure 1: Coupling calcium-responsive polymer brushes to graphene field-effect transistors.

Recent Publications

1. Berninger T, Bliem C, Piccinini E, Azzaroni O and Wolfgang Knoll W (2018) Cascading reaction of arginase and urease on a graphene-based FET for ultrasensitive, real-time detection of arginine. Biosens. Bioelectron. https://doi.org/10.1016/j.bios.2018.05.027.
2. Piccinini E, Alberti S, Longo G, Berninger T, Breu J, Dostalek J, Azzaroni O and Knoll W (2018) Pushing the boundaries of interfacial sensitivity in graphene FET sensors: polyelectrolyte multilayers strongly increase the Debye screening length. J. Phys. Chem. 122(18):10181–10188

3. Piccinini E, Bliem C, Reiner Rozman C, Battaglini F, Azzaroni O and Knoll W (2017) Enzyme-polyelectrolyte multilayer assemblies on reduced graphene oxide field-effect transistors for biosensing applications. Biosens. Bioelectron. 92:661-667.
4. Reiner Rozman C, Larisika M, Nowak C and Knoll W (2015) Graphene-based liquid-gated field effect transistor for biosensing: Theory and experiments. Biosens. Bioelectron. 70:21-7.

Biography

W Knoll earned his PhD degree in Biophysics from the University of Konstanz in 1976. From 1991-1999 he was the Laboratory Director for Exotic Nanomaterials in Wako, Japan, at the Institute of Physical and Chemical Research (RIKEN). From 1993 to 2008, he was Director at the Max Planck Institute for Polymer Research in Mainz, Germany. Since 2008, he is the Scientific Managing Director of the AIT Austrian Institute of Technology. Since 2010 he is a Regular Member of the Austrian Academy of Sciences. He received an Honorary Doctorate from the University of Twente, the Netherlands in 2011 and became a Member of the Academia Europaea in 2017.

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Notes:

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Day 2

Joachim Maier, Biosens J 2018, Volume 7
DOI: 10.4172/2090-4967-C1-001

Joachim Maier

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The connection between chemistry and electric function in solids

In loose terms chemistry is the chemistry of the perfect state (perfect crystallographic structure) plus chemistry of the excited state (defect structure). The latter is responsible for the electric transport and storage properties. In aqueous solutions this function is taken by H^+ and OH^- ions as well as dissolved ions. In solids this role is carried out by point defects such as excess (interstitials) and lacking particles (vacancies). It is exactly the consideration of point defect chemistry which is necessary to understand and tune ionic transport phenomena in solids hence forming the bridge between chemistry and electric function. This picture also comprises the electronic transport enabled by excess electrons and electron holes. It is shown how the charge carrier chemistry can be understood, analyzed and varied as a function of stoichiometry and doping not only in the bulk but also at interfaces. Of special interest are size effects on the electronic and ionic carrier concentrations. These defect-chemical considerations directly translate into the electric function in batteries, fuel cells and photo-electrochemical devices. This does not only hold at or near equilibrium, also the kinetic performance depend on such issues. In addition to transport-related questions, the point defects are most relevant acid-base or redox-active centers and are thus of central significance, not only for transport, but also for reaction kinetics and catalysis. A selection of applied examples such as storage modes in batteries, reaction kinetics in fuel cells or transport effect in photo-perovskites will be addressed.

Recent Publications

1. Maier J (2005) Nanoionics: ion transport and electrochemical storage in confined systems. Nature Materials 4:805–815.
2. Maier J (2013) Thermodynamics of electrochemical lithium storage. Angewandte Chemie International Edition 52:4998–5026.
3. Chen C C, Fu L J and Maier J (2016) Synergistic, ultrafast mass storage and removal in artificial mixed conductors. Nature 536:159–164.
4. Zhu C, Usiskin R, Yu Y and Maier J (2017) The nanoscale circuitry of battery electrodes. Science DOI: 10.1126/science.aao2808.
5. Yang T Y, Gregori G, Pellet N, Grätzel M and Maier J (2015) The significance of ion conduction in a hybrid organic–inorganic lead-iodide-based perovskite photosensitizer. Angewandte Chemie International Edition 54:7905–7910.

Biography

Joachim Maier studied Chemistry at the University of Saarbrücken, received his PhD in 1982 from the same university and completed his Habilitation at the University of Tübingen in 1988. He has lectured at the University of Tübingen, at Massachusetts Institute of Technology as a foreign Faculty Member, at the University of Graz as a Visiting Professor, and at the University of Stuttgart as an Honorary Professor. He is Past President of the International Society of Solid State Ionics. As Director of the Physical Chemistry Department (since 1991) of the Max Planck Institute for Solid State Research and Member of various national and international academies his concern is the conceptual understanding of chemical and electrochemical phenomena involving solids as well as their use in materials science. He has been listed as one of the most influential scientific minds (Thomson Reuters).

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Jelena Popovic, Biosens J 2018, Volume 7
DOI: 10.4172/2090-4967-C1-001

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Interfacial effects and charge carrier chemistry in lithium electrolytes

Lithium electrolytes that link high ionic conductivities with high lithium transference number are rare, and believed to be essential for functional high power batteries. One effective way to prepare such materials is by engaging an interfacial effect on an oxide surface in order to demobilize the anion in liquid/solid electrolytes. The galvanostatic polarization experiments as well as the influence of surface area, salt concentration and temperature on their outcome will be discussed in details. Furthermore, significance of interfacial effects in other ionic devices will be touched upon. Rather than just facilitating high performance materials, liquid/solid electrolytes are a fruitful playground for fundamental understanding of the electrical double layer. A model glyme on muscovite mica system is a starting point for tackling the issue of ion-ion correlations in concentrated electrolytes and its effect on the Debye lengths estimated from the surface force measurements. Finally, solid polymer lithium electrolytes can be used in bilayer graphene gating experiments. Here, the electrolyte plays a vital role in the direct measurement of the high lithium diffusion coefficient.

Recent Publications

1. Pfaffenhuber C, Göbel M, Popovic J and Maier J (2013) Soggy-sand electrolytes: status and perspectives. Physical Chemistry Chemical Physics 15(42):18318-35.
2. C Pfaffenhuber, F Hoffmann, M Fröba, J Popovic and J Maier (2013) Soggy sand effects in liquid composite electrolytes with mesoporous materials as fillers. Journal of Materials Chemistry A 1(40):12560-67.
3. J Popovic, G Hasegawa, I Moudrakovski and J Maier (2016) Infiltrated porous oxide monoliths as high lithium transference numbers. Journal of Materials Chemistry A 4(19):7135-40.
4. F Bella, J Popovic, A Lamberti, E Tresso, C Gerbaldi and J Maier (2017) Interfacial effects in solid-liquid electrolytes for improved stability and performance of dye-sensitized solar cells. ACS Applied Materials and Interfaces 9(43):37797-37803.
5. M Kühne, F Paolucci, J Popovic, P M Ostrovsky, J Maier and J H Smet (2017) Ultrafast lithium diffusion in bilayer graphene. Nature Nanotechnology 12:895-900.

Biography

Jelena Popovic is a Scientist at the Max Planck Institute for Solid State Research in Stuttgart, Germany since 2011. Her academic background includes a degree in Chemical Engineering from the University of Belgrade, Serbia in 2008 and a PhD in Colloid Chemistry from University of Potsdam/Max Planck Institute for Colloids and Interfaces in Potsdam, Germany in 2011. Her scientific interests range from new materials and transport mechanisms in ionic materials to soft matter electrochemistry and sustainable synthesis of nanomaterials.

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