

MM 26: Materials for Energy Storage and Conversion

Sessions: Li-Batteries and Alternative Concepts

Time: Wednesday 15:00–18:15

Location: H43

MM 26.1 Wed 15:00 H43

Studying the cycling behavior of Silicon thin-film battery electrodes by in-situ quartz crystal microbalance — ●TOBIAS KOHLER, EFI HADJIXENOPHONTOS, and GUIDO SCHMITZ — Chair of Material Physics, Institute of Materials Science, University of Stuttgart, Heisenbergstraße 3, 70569 Stuttgart, Germany

A quartz crystal microbalance (QCM) is able to detect mass changes in the nanogram region. This makes it suitable to monitor the lithiation and delithiation of battery electrodes. Some particle-binder composite electrodes were already researched by means of QCM. However, investigations of thin-films are scarce. Here, amorphous silicon electrodes were ion beam sputter deposited onto the front electrode of the quartz crystal. By combining the QCM results with the cyclic voltammetry (CV), a variety of information can be gained. This includes a mass per charge ratio, which is similar to a conventional mass spectrometry. It opens the possibility to measure the growth of the solid electrolyte interface (SEI) and determine the species that are included therein. Different thicknesses of silicon are investigated to see the effect on the SEI layer growth. The results of the QCM are compared to electron microscopy and X-ray photoelectron emission spectra observations.

MM 26.2 Wed 15:15 H43

Electrochromism and Phase Transformation in Lithium Titanate — ●YUG JOSHI, EFI HADJIXENOPHONTOS, and GUIDO SCHMITZ — Chair of Materials Physics, Institute of Material Science, University of Stuttgart, Stuttgart, Germany

Lithium titanate (LTO) is a well-known battery anode mainly due to its high rate capability, high cyclability and high power density. In the potential range between 1V-2V vs Li/Li⁺, intercalation appears between two phases i.e. Li₇Ti₅O₁₂ (stable below ca. 1.55V) and Li₄Ti₅O₁₂ (stable above ca. 1.55V). While there is negligible volumetric change, the two phases show contrasting dielectric constants and complex refractive indices. Our study is based on understanding the phase transformation mechanism of LTO by exploiting these contrasting properties in the two phases. To realize this, firstly the active LTO layer is deposited using ion beam sputtering and annealed appropriately. The crystal structure of the layers are probed using X-ray diffraction and transmission electron microscopy. Once the crystal structure is confirmed, the samples are electrochemically characterized. Finally, the electrochromic characterization is performed in-situ and ex-situ to visualize the electrochromic reversibility and to extract the complex refractive indices. The latter are used to calculate the dielectric constants in the single- and in the dual-phase regions. Describing the dielectric constant of the dual phase region as a combination of those of the pure phases, information is derived about the migration of the phase front during transformation.

MM 26.3 Wed 15:30 H43

Electrochemical and Microstructural Analysis of High-capacity Li-Mn-O Thin Film Battery Electrodes — ●HENRY MÜLLER, YUG JOSHI, EFI HADJIXENOPHONTOS, CLAUDIA PETER, and GUIDO SCHMITZ — Institute of Materials Science, Chair for Materials Physics, University of Stuttgart, Heisenbergstraße 3, 70569 Stuttgart, Germany

Research worldwide has taken on the challenge to develop new electrode materials for cost-efficient, reliable batteries with higher capacities. We present a sputter-deposited thin film cathode made from manganese oxide with up to three times the capacity observed in comparable conventional LiMnO electrodes from the well-known spinel structure. The novel microstructure, domains of rock salt, monoclinic and spinel crystal structures, unlocks the voltage range from 2V to 4.4V vs. Li for long term cycling at the capacity of 225 mAh/g. We characterize the material on the nano-scale using high-resolution transmission electron microscopy and electron diffraction. Furthermore, we investigate the influence of oxygen deficiency on the capacity and electrochemical behavior of the electrode. The in-situ tailoring of electrode properties is possible by controlling the oxygen partial pressure during deposition.

MM 26.4 Wed 15:45 H43

Analytical Transmission Electron Microscopy studies of

LiNi_xMn_yCo_{1-x-y}O₂ and Silicon electrode materials for lithium ion batteries — ●ARDAVAN MAKVANDI¹, MARTIN PETERLECHNER¹, SIMONE CASINO², TOBIAS GALLASCH², MARTIN WINTER², and GERHARD WILDE¹ — ¹Institute of Materials Physics, University of Münster, Münster, Germany — ²MEET Battery Research Center, University of Münster, Münster, Germany

The modification of state-of-the-art electrode materials by nanostructured coatings is one approach to optimize crucial parameters for application, such as electronic conductivity or mechanical stability of the raw materials. In general, interfaces (active material/coating; electrode surface/electrolyte) determine the local Li ion transport kinetics and finally the electrochemical cell performance in terms of cycling stability or capacity retention. Therefore, it is necessary to study the structure and chemistry of electrodes and electrode/electrolyte interfaces. In this work, the structural and chemical evolution in the bulk and surface regions of LiNi_xMn_yCo_{1-x-y}O₂ (NMC) and silicon thin film electrodes after lithiation and de-lithiation processes is studied using scanning transmission electron microscopy (STEM) imaging, electron diffraction, and electron energy loss spectroscopy (EELS). In case of EELS quantification, the Mn-M edge overlaps with the Li-K signal hindering the direct measurement of the lithium content. Nonetheless, by using EELS, the valence states of transition metals (Mn, Co, and Ni) and consequently an indirect measurement of the lithium ion distribution in the NMC cathode materials can be obtained.

MM 26.5 Wed 16:00 H43

Investigation of micro batteries containing single secondary particles of Li(Ni_{1-x-y}Co_xMn_y)O₂ as cathode material — ●MARKUS SEBASTIAN FRIEDRICH^{1,2}, SIMON BURKHARDT^{1,2}, MATTHIAS THOMAS ELM^{1,2,3}, and PETER JENS KLAR^{1,2} — ¹Institute of Experimental Physics I, Heinrich-Buff-Ring 16, 35392 Giessen — ²Center for Materials Research (LaMa/ZfM), Heinrich-Buff-Ring 16, 35392 Giessen — ³Institute of Physical Chemistry, Heinrich-Buff-Ring 17, 35392 Giessen

Lithium ion batteries (LIBs) are today's state-of-the-art power supplies for portable electronic devices as well as for electrical and hybrid vehicles. To optimize such battery systems, a deeper understanding of the transport in the active material used in the electrodes of LIBs is essential. Typically layered structured transition metal oxides, such as Li(Ni_{1-x-y}Co_xMn_y)O₂ (NCM), are used as cathode active materials. Conventionally, for investigation, micrometer sized secondary particles of the active material, built from a complex porous network of nanometer sized single crystalline primary particles, are incorporated in to composite electrodes, which contain additives that might influence or superpose the properties of the pure active material.

We developed a technique to assemble micro batteries that contain single secondary particles of NCM and performed electrochemical measurements on such cell systems. In the course of these investigations, we found clear evidence that the transport in the active material particles depends on the secondary particle diameter and, therefore, depends on the porous primary particle network.

MM 26.6 Wed 16:15 H43

poly(10-(4-styrene)-N-10H-phenothiazine) (PS-N-PT) as organic redox-active cathode materials for lithium-ion batteries — ●YUQUAN WU¹, FABIAN OTTENY², BIRGIT ESSER², and RÜDIGER KLINGELER¹ — ¹Kirchhoff-Institute for Physics, Heidelberg University, 69120 Heidelberg, Germany — ²Institut für Organische Chemie, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany

Organic redox-active materials provide an environmentally friendly alternative to traditional inorganic electrode materials for lithium ion batteries. Due to structural stability and high-cycling performance, redox-active organic polymers are competitive candidates in this respect. We report electrochemical studies on the redox-active polymer poly(10-(4-styrene)-N-10H-phenothiazine) which is investigated with respect to its feasibility as cathode material. Cyclic voltammetry shows two pairs of redox peaks centered at 3.6 and 4.2 V, respectively, with a separation of 0.05 V. Changes of redox behavior between 1st and 2nd cycle indicate conformational changes on the polymer structure upon the first cycle at high voltage range of 4 - 4.5 V which cause elec-

trochemical activation of the material. Galvanostatic cycling of the activated material between 3 and 4 V shows capacity amounts to 72 mAhg⁻¹ in cycle 2 and capacity retention of 85% by cycle 100.

15 min. break

MM 26.7 Wed 16:45 H43

Investigation of the stoichiometry of $Ce_{1-x-y}Pr_xZr_yO_{2-\delta}$ single crystals — ●JUREK LANGE¹, KATHRIN MICHEL², GREGOR ULBRICH³, MARBIN LERCH³, SANGAM CHATTERJEE¹, MATTHIAS ELM¹, and DETLEV HOFMANN¹ — ¹Institute of Experimental Physics I and Center for Materials Research, Heinrich-Buff-Ring 16, Justus-Liebig-University Giessen, D-35392 Giessen, Germany — ²Institute of Physical Chemistry, Heinrich-Buff-Ring 17, Justus-Liebig-University Giessen, D-35392 Giessen, Germany — ³Institute of Chemistry, Technical University Berlin, Strasse des 17. Juni 135, D-10623 Berlin, Germany

The solid solution of ceria and praseodymia is interesting, as oxygen storage capacity and electrical conductivity are enhanced at the intermediate temperature range. Thus, we investigated single crystals of $Ce_{1-x-y}Pr_xZr_yO_{2-\delta}$ grown by the skull melting technique and powders of the binary compounds $CeO_{2-\delta}$ and $Pr_6O_{11-\delta}$ by electron paramagnetic resonance (EPR) and photo-EPR experiments. The methods are able to identify and to determine the energy positions of recharging levels in respect to the valence and conduction band of the material. In the as prepared samples we observe the characteristic spectrum of Pr^{4+} caused by the interaction of the unpaired 4f electron and the nuclear spin of $I = 5/2$ (abundance 100%). We followed the evolution of the spectra upon annealing which effects the oxygen in the material.

MM 26.8 Wed 17:00 H43

Rational surface engineering toward optimizing hydrogen evolution activity of nanoporous electrodes — ●LONG LIU, HUAPING ZHAO, YANG XU, CHENGLIN ZHANG, YAOGUO FANG, and YONG LEI — Institut für Physik & IMN MacroNano (ZIK), Technische Universität Ilmenau, 98693, Ilmenau, Germany

A rational surface engineering strategy for nanoporous electrodes is demonstrated to promote the hydrogen evolution (HER) process. Cobalt nanopore arrays (CoNPA) were fabricated as a representative HER electrode and subsequently functionalized by a conformal ultrathin titanium dioxide (TiO₂) with optimized thickness and thereafter a well-dispersed platinum (Pt) nanoparticles with an ultralow mass loading (ca. 54 μg cm⁻²) anchored on TiO₂ layer. The advanced features of nanoporous architecture, the improved wettability by TiO₂ layer, and the abundant reactive sites arising from well-dispersed Pt nanoparticles synergistically contribute to enhance the HER kinetics of CoNPA electrodes in alkaline conditions, and finally achieved low overpotential of 29 mV, small Tafel slope of 42 mV per decade as well as long-termed performance and structure stability. Not limited to the HER electrodes, the similar strategy is also expected to be further applied to design nanoelectrodes for other electrochemical energy conversion and storage devices.

MM 26.9 Wed 17:15 H43

On the proper characterization of OER catalysts: The role of experimental and preparation parameters — ●SABITA BHANDARI¹, PRAVEEN NARANGODA¹, MARC TESCH¹, IOANNIS SPANOS¹, ROBERT SCHLÖGL^{1,2}, and ANNA MECHLER¹ — ¹Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr — ²Fritz Haber Institute of the Max Planck Society, Berlin

For kinetically slow oxygen evolution reaction (OER), the use of a catalyst is essential to make it energetically efficient and many research works on finding a novel catalyst are ongoing. Nowadays, operando studies - utilizing various techniques - are carried out to obtain a fundamental understanding of the intrinsic catalytic properties. However, how a catalyst performs under an oxidative condition of OER is determined not only by its intrinsic catalytic property but also by some experimental parameters. Generally for a powdered sample, catalyst ink is made with a suitable binder and deposited as thin layers on electrode substrate and subsequently, the electrochemical analysis is carried out in an electrolyte solution of choice. So, factors such as the electrode substrate, binder, electrolyte impurities, pH and concentration, type of gas saturated in electrolyte etc. might affect the overall performance of a catalyst. These parameters are important as these can affect the

true active species formed during electrocatalysis.[1],[2] In this study, we give an overview of the influence of some of the above-mentioned factors on the catalytic performance of a commercially available NiCo oxide for OER. [1] J. Electrochem. Soc., 2015, 162(10), F1144-F1158. [2] J. Electrochem. Soc., 2015, 162(12), F1384-F1396.

MM 26.10 Wed 17:30 H43

Photo-electrochemical properties of GaNP epitaxial films grown by MOCVD — ●RENÉ COUTURIER¹, PETER LUDEWIG², WOLFGANG STOLZ^{2,3}, KERSTIN VOLZ³, SANGAM CHATTERJEE¹, and DETLEV M. HOFMANN¹ — ¹Institute of Experimental Physics I, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen, Germany — ²NAsPIII/V GmbH, Am Knechtsacker 19, D-35041 Marburg, Germany — ³Faculty of Physics and Materials Sciences Centre, Philipps-Universität Marburg, Hans-Meerwein-Str. D-35032 Marburg, Germany

Efficient charge transfer at the semiconductor-electrolyte-interface is very crucial for photo-electrochemical applications like water splitting. A very promising material for such electrochemical applications are Ga_{1-x}N_xP semiconductor films. The films show charge-carrier injection under irradiation into the electrolyte, depending on the applied bias. Electron- and hole-transfers are achieved. The processes are investigated by wavelength dependent photocurrent measurements under applied potentials. In parallel, the emission properties of the material are investigated which dominantly show the recombination via clusters of nitrogen dopants. The results are discussed in the frame of the surface band-bending model.

MM 26.11 Wed 17:45 H43

A gasochromic Back Reflector for a Switchable Ultra-Thin Germanium Solar Cell — ●MAXIMILIAN GÖTZ, MAREN LENGERT, NORBERT OSTERTHUN, KAI GEHRKE, MARTIN VEHSE, and CARSTEN AGERT — DLR-Institut für Vernetzte Energiesysteme e.V. Carl-von-Ossietzky-Str. 15 26129 Oldenburg

Magnesium-Palladium (Mg/Pd) layers are gasochromic materials, which undergo a reversible phase change from a metallic-reflective into a dielectric-transparent state upon hydrogen exposure.

In this contribution we present this layer stack as a switchable mirror for use in a Fabry-Pérot absorber. This is used to modify an ultra-thin amorphous Germanium solar cell into a switchable photovoltaic device. Germanium is placed between a transparent conductive oxide and the gasochromic switchable layer, which is used as a back reflector. Due to Hydrogen exposure the cavity resonance is decreased to single pass absorption and the layer stack becomes transparent.

Optical and material properties of the cavity are characterized by in-situ spectroscopy and ellipsometry during the switching process. Optical simulations are used to adjust the thicknesses and refractive indices of the resonator materials for optimized field enhancement in the Germanium absorber. The electrical properties of Mg/Pd as back-contact for solar cell applications are discussed and the diode behavior of the cell under illumination in reflective and transparent state is shown.

MM 26.12 Wed 18:00 H43

Experimental study on the electronic structure of ZrNiSn half-Heusler thermoelectric material — ●CHENGUANG FU¹, MENGUYU YAO¹, L. Z. MAULANA², GUDRUN AUFFERMANN¹, GERHARD FECHER¹, M. DRESSEL², A. V. PRONIN², and CLAUDIA FELSER¹ — ¹Max Planck Institut für Chemische Physik Fester Stoffe, 01187 Dresden, Germany — ²Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart, Germany

ZrNiSn-based half-Heusler compounds have been developed as good thermoelectric materials in the past decades, which are believed to be attributed to their excellent electrical power factor. However, there is still very few direct experimental investigation of the intrinsic electronic structure for this system, which actually is significant to understand the origin of their excellent thermoelectric properties. In this work, we have successfully grown high-quality undoped and doped ZrNiSn single crystals. With these crystals, we were able to measure their optical reflectivity in the frequency range from 80 cm⁻¹ to 18000 cm⁻¹ and to perform a systematic high-resolution ARPES study on their intrinsic electronic structure. It is found that the band gap of ZrNiSn single crystals is about 0.5 ~ 0.6 eV, which is in agreement with the DFT calculations result, but much larger than the value of 0.2 ~ 0.3 eV previously reported in polycrystalline samples. The possible reasons for this difference will be discussed.