

O 80: SYLI: Symposium Interfacial Challenges in Solid-State Li Ion Batteries - Structure - property relationships II

Time: Wednesday 15:45–16:45

Location: IFW D

O 80.1 Wed 15:45 IFW D

Process monitoring of charging/discharging of lithium ion battery cathodes by operando SQUID magnetometry — •ROLAND WÜRSCHUM¹, GREGOR KLINSER¹, STEFAN TOPOLOVEC¹, HARALD KREN², STEFAN KOLLER², WALTER GOESSLER³, and HEINZ KRENN⁴ — ¹Inst. of Mater. Phys., Graz Univ. of Technology, Graz, Austria — ²VARTA Micro Innovation GmbH, Graz — ³Inst. of Chem., Univ. Graz — ⁴Inst. of Phys., Univ. Graz

The magnetic susceptibility χ of cathode materials, which contain transition metals, substantially changes during charging/discharging and, therefore, serves as highly sensitive fingerprint for the charge state. A novel pathway in this direction has recently opened up by developing in-situ electrochemical techniques for magnetometry. Operando magnetic χ -measurements on Li_xCoO_2 [1] and $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) cathode materials [2] in a SQUID magnetometer during repetitive electrochemical cycling were performed enabling a continuous and bulk sensitive monitoring of the charge compensation process. Upon charging of NMC up to Li contents of $x = 1/3$ exclusively Ni undergoes oxidation, namely in two consecutive steps $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ for $x > 2/3$ and $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$ for $2/3 > x > 1/3$ [2]. Co oxidation for $x < 1/3$ is found to be irreversible [2]. In the case of Li_xCoO_2 , evidence is found for a nonmetal–metal transition of Anderson–type [1]. In addition to Co also O undergoes partial oxidation, as also observed for NMC.

[1] St. Topolevec et al., *J. Sol. State Electrochem.* 20 (2016) 1491.

[2] G. Klinser et al., *Appl. Phys. Letters* 109 (2016) 213901.

O 80.2 Wed 16:00 IFW D

Enhancement of Sodium Ion Battery Performance Enabled by Oxygen Vacancies — •YANG XU, MIN ZHOU, CHENGLIANG WANG, LIYING LIANG, FABIAN GROTE, YAN MI, and YONG LEI — Institute für Physics & IMN MacroNano (ZIK), Technische Universität Ilmenau, Ilmenau 98693, Germany

The utilization of oxygen vacancies (OVs) in sodium ion batteries (SIBs) is expected to enhance performance, yet it has rarely been reported. Taking the $\text{MoO}_3\text{-x}$ nanosheet anode as an example, for the first time we demonstrate the benefits of OVs on SIB performance. Moreover, the benefits at deep-discharge conditions can be further promoted by an ultrathin Al_2O_3 coating. Ex-situ electrochemical impedance and X-ray photoelectron spectroscopy measurements show that the OVs increase the electric conductivity and Na-ion diffusion coefficient, and the promotion from ultrathin coating lies in the effective reduction of cycling-induced solid-electrolyte interphase. The coated nanosheets exhibited high reversible capacity and great rate capability with the capacities of 283.9 mAh g⁻¹ at 50 mA g⁻¹ and 179.3 mAh g⁻¹ at 1 A g⁻¹ after 100 cycles. This work could not only arouse future attention on OVs for sodium energy storage, but also open up new possibilities for designing strategies to utilize defects in other energy storage systems.

Reference

Y. Xu, M. Zhou, X. Wang, C. Wang, L. Liang, F. Grote, M. Wu, Y.

Mi, Y. Lei, *Angew. Chem. Int. Ed.* 2015, 54, 8768.

O 80.3 Wed 16:15 IFW D

Polycrystalline Na_xCoO_2 thin films on β -Alumina ceramics for solid state batteries — •PHILIPP KEHNE¹, CONRAD GUHL², RENÉ HAUSBRAND², and PHILIPP KOMISSINSKIY¹ — ¹Department of Materials Science, TU-Darmstadt, Advanced thin film technology — ²Department of Materials Science, TU-Darmstadt, Surface science

Good cycling performance was previously shown for rechargeable sodium ion batteries with layered-oxide cathode materials such as Na_xCoO_2 in combination with liquid electrolytes. However, studies of sodium-based solid state batteries are necessary to correlate the electronic structure of sodium-ion insertion materials with the battery performance. Here we report polycrystalline Na_xCoO_2 films grown on β -Alumina polycrystalline ceramic substrates with pulsed laser deposition. The sodium content in the films can be adjusted in the range of $x = 0.6 \cdot 1.1$ by varying the post-deposition annealing conditions. The β -alumina substrates reveal ionic conductivities of 0.002 S/cm (25 °C) and can be used as electrolyte in solid-state sodium batteries. The fabricated Swagelok-type rechargeable batteries with Na_xCoO_2 thin-film cathodes, β -alumina electrolyte, and sodium anodes reveal an open circuit voltage of 2.75 V and a specific capacitance of $C = 80$ mAh/g. Investigations of the electronic structure of the materials and interfaces in the fabricated batteries by in-situ XPS are in progress.

O 80.4 Wed 16:30 IFW D

Large-scale highly ordered Sb nanorod arrays anode with high capacity and rate capability for sodium-ion batteries — •LIYING LIANG, YANG XU, CHENGLIANG WANG, LIAOYONG WEN, YAOGUO FANG, YAN MI, MIN ZHOU, HUAPING ZHAO, and YONG LEI — Institute for Physics and IMN MacroNano, Ilmenau University of Technology, Ilmenau 98693, Germany.

The poor electrochemical performance of Na-ion batteries is the major bottleneck for future development. Hence a performance-oriented electrode structure is proposed, which is 1D nanostructure arrays with large-scale high ordering, well vertical alignment, and large interval spacing. Benefiting from these structure merits, a great enhancement on electrochemical performance could be achieved. To Sb as an example, we firstly report large-scale highly ordered Sb nanorod arrays with uniform large interval spacing (190 nm). In return for this electrode design, high ion accessibility, fast electron transport, and strong electrode integrity are presented here. Used as additive-free anode for SIBs, Sb nanorod arrays showed a high capacity of 620 mAh g⁻¹ at the 100th cycle with a retention of 84% up to 250 cycles at 0.2 A g⁻¹, and superior rate capability for delivering reversible capacities of 579.7 and 557.7 mAh g⁻¹ at 10 and 20 A g⁻¹, respectively. A full cell coupled by P2-Na₂/3Ni₁/3Mn₂/3O₂ cathode and Sb nanorod arrays anode was also conducted, which showed a good cycle performance up to 250 cycles, high rate capability up to 20 A g⁻¹, and large energy density up to 130 Wh kg⁻¹.