

# Americas International Meeting on Electrochemistry and Solid State Science 2018

**Battery highlights include lithium metal anodes, solid state conductive materials, interface engineering and electrolyte additives**

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## Introduction

The Americas International Meeting on Electrochemistry and Solid State Science was a joint international conference of the 234th Meeting of The Electrochemical Society (ECS), the XXXIII Congreso de la Sociedad Mexicana de Electroquímica (SMEQ) and the 11th Meeting of the Mexico Section of the Electrochemical Society. It was well attended with worldwide representation including industrial organisations such as BASF (Germany), Toyota (Japan), Umicore (Belgium), Tanaka (Japan), Johnson Matthey (UK) and a wide range of academics. The conference contained up to twenty-five parallel sessions. The original searchable conference programme is available online.

This selective review discusses some of the talks presented in the following sessions:

- A01 Battery and Energy Technology Joint General Session
- A02 Challenges in Novel Electrolytes, Organic Materials, and Innovative Chemistries for Batteries
- A04 Lithium-Ion Batteries
- A05 Beyond Lithium-Ion Batteries
- A06 Electrolytes and Interfaces in Lithium-Ion Batteries
- I02 Solid State Ionic Devices

## Batteries and Battery Materials

'Open-Software Tools for the Analysis of Electrochemical Impedance Spectra' by M. D. Murbach and D. T. Schwartz (University of Washington, USA), presented electrochemical impedance spectroscopy analysis *via* open source Python code. The code is available from GitHub (USA) to be freely pip installed as 'impedance.py'. Within the new code there are functions that have been created which simplify coding and the analysis allows new user impedance models to be integrated using 'fit' and 'predict'. Altair declarative visualisation in Python was used to aid understanding of data and prepare graphics. Furthermore, a web-based physics-based electrochemical impedance model is currently under development and the current version is freely accessible as 'Impedance Analyzer' (1).

'Multiphase Porous Electrode Theory' by R. B. Smith and M. Z. Bazant (Massachusetts Institute of Technology, USA), presented the open source software multiphase porous electrode theory (MPET). Non-equilibrium thermodynamics models of porous electrodes (2) previously described in the literature were considered for generating an active material model. This was expanded to allow addition effects such as stress effects and other variables beyond merely the concentration parameter. The Newman model was compared with the phase field model. The phase field model suggests that surface concentration remains high for a phase segregating particle and provides different predictions about failure modes such as lithium plating at carbon anodes. Reaction rate models such as Butler-Volmer and Marcus-Hush were compared next (3). It was proposed that some use

of 'film resistance' may otherwise be attributable to a Marcus-Hush-Chidsey (MHC) mechanism. To illustrate this the graphite thermodynamic model using Butler-Volmer model with film contributions was applied to single particle real-time delithiation experimental data (4). This work was subsequently applied to Samsung electrodes with data collected by Samsung (South Korea) and Samsung Advanced Institute of Technology (SAIT, South Korea). This model accurately described the surface concentrations measured. Although the timescales with the Butler-Volmer film model were also shown to match experiment for lithium iron phosphate (LFP) polarisation, Marcus type kinetics were able to more accurately match the polarisation curvature. Thus, although metallic like materials can be modelled with Butler-Volmer film-type model, MHC kinetics extended to concentrated solutions should be considered for non-metallic materials.

'Use of Lithium Iron Phosphate (LFP) Batteries as Piezoelectrochemical Materials to Increase Low-Frequency Mechanical Energy Harvesting' by J. I. Preimesberger, S. Kang and C. B. Arnold (Princeton University, USA), described the ideal concept device which is anticipated to provide a flat voltage profile with suitable expansion of at least one electrode to provide the necessary voltage effect due to strain. Having a low change in potential with respect to charge helps with energy harvesting though LFP is not initially the obvious choice if based on the resulting comparison of coupling constants with lithium nickel manganese cobalt oxide/silicon (NMC/Si) or lithium cobalt oxide/graphite (LCO/G) batteries. Cycling was performed at 8 MPa mechanical energy harvesting at 28  $\mu$ Hz and 10 hours per cycle. Actual output was on the order of 0.1–0.4 mV using a 10  $\Omega$  resistor. Higher K yields a higher potential output whereas lower differential voltage (dV/dQ) yields a longer power output. The author utilised commercial cells for ease of set up.

'Solid State Organic Ionic Plastic Crystals and Composite Materials for Energy Storage' by P. C. Howlett *et al.* (Deakin University, Australia), demonstrated the use of organic ionic plastic crystals (OIPCs) as solid electrolytes compatible with lithium metal. Typically, OIPCs use similar anions to those of ionic liquids, though the anions are usually symmetric. An archetypal OIPC is  $P_{1224}^+PF_6^-$  in which differential scanning calorimetry showed four solid phases with 1 mS  $cm^{-1}$  conductivity in phase one at 120–150°C just prior to melt. Addition of an anion matched lithium salt resulted in two-phase formation with a liquid phase

that percolates through the solid with similar high conductivities observable as low as 20°C. This sort of material was applied to a lithium ion battery construction to yield reasonable performance (5). Unfortunately, these materials are too soft to serve as a standalone solid separator so ceramic particles were added to improve mechanical strength however lithium ion mobility was hindered due to particle surface confined lithium concentration. The lithium transference number in these systems was measured between 0.1–0.44. Polymer (polyvinylidene fluoride) particles were coated with OIPC and used to construct LFP and NMC cells with improved lifetime under normal and accelerated test conditions (6, 7). This work was also extended to sodium-doped OIPCs.

'A Route to High Energy Density Co-free Cathode Materials' by G. Ceder (University of California, Berkeley, USA) discussed rock-salt materials as Li-ion cathodes which can percolate at only 10% lithium excess. The probed metal chemistries included manganese, iron, vanadium, nickel with molybdenum, niobium, titanium, zirconium used for charge compensation. The deformation modes of the octahedra into normal modes showed that  $d^0$  elements are most suitable due to accommodating distortion (8). For example with  $Li(Ni_{0.5}Ti_{0.5})O_2$  vs.  $Li(Ni_{0.5}Mn_{0.5})O_2$ , the Ti-based material was claimed as impossible to make ordered while the Mn-based material was very difficult to make disordered. Excellent transmission electron microscopy (TEM) micrographs were shown which visualised the diffusion channels for a disordered rock-salt material. However, lithium excess and disorder can lead to oxygen redox activity. By fluorinating, the same lithium excess could be utilised while maintaining a higher level of transition metal thus reducing the oxygen redox capacity. For example  $(Li_{1+x}M_{1-x})(O_{2-y}F_y)$  was successfully prepared at up to  $y = 0.2$  and differential electrochemical mass spectrometry data showed less than 25% oxygen loss (9). The author utilised an interesting approach for materials design by *ab initio* calculation of ternary phase diagrams of lithium fluoride, metal oxides and charge compensators (i.e. lithium niobite). High energy ball milling was used to prepare  $Li_2Mn_{2/3}Nb_{1/3}O_2F$  which gave negligible oxygen evolution on charging up to 5 V (10). This approach was anticipated to provide up to 1000 Wh  $kg^{-1}$ . When queried on mobility of  $d^0$  elements during operation, the author noted that dissolution issues were seen with  $Mo^{6+}$  but not  $Ti^{4+}$  or  $Nb^{5+}$ .

'Multiscale Simulation of the Fabrication Process of Lithium Ion Battery Electrodes' by A. A. Franco

*et al.* (CNRS, France) presented results from the European Research Council (ERC) Project 'ARTISTIC'. Slurries are challenging to model as one should include electrostatic forces, Van der Waals, steric, hydrodynamic and Brownian forces, as well as multiple size scales from 1 nm to 100 nm to 10  $\mu\text{m}$ . Coarse grained classical molecular dynamics was applied (LAMMPS 1/1000 in volume) to construct an 'equilibrated slurry' containing NMC, carbon, binder and solvent. Artificial intelligence was utilised to parametrise the force fields to match experimental results such as viscosity as a function of shear rate. Drying of layers was simulated which interestingly showed higher porosity for near maximised active material content at 95% (11). Subsequently, the dry layer was 'meshed' in order to solve the Newman model related equations to explicitly solve the battery electrochemical performance. Capacity cycling was predicted and confirmed to yield capacity ranking 85% > 90% > 95% active material content. Excellent results with fine grained resolution of lithium concentration in the active material were determinable at any state of charge with less than 10% uncertainty. The model is anticipated to be published open source sometime during 2019.

'New Battery Chemistries enabled by Advanced Aqueous, Non-aqueous and Hybrid Electrolytes' by K. Xu (US Army Research Laboratory, USA) identified fluorosolvents, sulfones and bisalt ethers as useful groups to enable new electrode materials. The battery materials interfaces (solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI)) were attributed as extending the electrochemical stability window of a given solvent by better matching the lowest unoccupied molecular orbital (LUMO) at an SEI and the highest occupied molecular orbital (HOMO) at the CEI. To manipulate the interphase, super concentration could be used or a HOMO/LUMO affecting additive. Fluorine source for interphases can be derived from fluoroethylene carbonate (FEC), 3,3,3-fluoroethylmethyl carbonate (FEMC) or 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether (HFE). Using 1 M  $\text{LiPF}_6$  in FEC:FEMC:HFE performance cycling with symmetric lithium metal revealed greater than 99.2% coulombic efficiency (CE) over 500 cycles with ultra-low overpotential. The same electrolyte was used in a Li/NMC 811 cell with 90% capacity retention at 450 cycles with 99.93% CE. With lithium cobalt phosphate/lithium (LCP/Li) the electrolyte enabled 93% capacity retention over 1000 cycles and greater than 99.9% CE. Investigation of these interfaces was

published recently. Next the author considered the high voltage conversion material iron(III) fluoride ( $\text{FeF}_3$ ) showing very high CE with greater than 400  $\text{mA g}^{-1}$  capacity over 1000 cycles (12). Next sulfolane data exhibited greater than 75% capacity retention at the 1000th cycle for a few battery chemistries (13). Water and non-aqueous electrolyte hybrid mixtures have been employed which enable a 4 V electrochemical stability window (14).

'Dual Coatings, Triple the Benefit: A Study in ALD Surface-Modifications to Nickel-Rich Architectures' by B. K. Hughes *et al.* (Forge Nano, USA) provided examples based on improvements on the state of the art. Data for improved LCO was demonstrated with niobium coating. Coated NMC was demonstrated to obtain lifetime and high potential operation. The cell total lifetime benefited further with an atomic layer deposition (ALD) coated graphite anode (cycled 6C:1C). Metal dissolution analysis was used to show that though little effect was seen during the first 25 cycles, much less dissolved cobalt was found after 100 cycles. Comparison of coated NMC vs. pristine NMC found no change to manganese and nickel dissolution.

' $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  Dry-Coated with Nano-Alumina as Positive Electrode Material' by L. Zheng and M. N. Obrovac (Dalhousie University, Canada) presented a coating method designed to modify surface chemistry, to suppress transition metal dissolution and to scavenge fluoride ions. The dry coating method was referred to as mechanofusion. It is designed to impact small particles onto the surface of larger particles (15). NMC 622 was coated with a dense layer of 3% aluminium oxide ( $\text{Al}_2\text{O}_3$ ) for 30 minutes at 1400 rpm mechanofusion. The process reduced the material density from 4.78  $\text{g cm}^{-3}$  to 4.34  $\text{g cm}^{-3}$  and reduced the Brunauer, Emmett and Teller (BET) surface area by half. Scanning electron microscopy (SEM) results illustrated that the surface coating was retained after ink and electrode processing. Cycling performance showed 100% capacity retention after 60 cycles (16).

'Rational Design of 3-D Current Collectors and Interfaces for Stabilized Li Metal Anodes' by K. H. Chen, A. J. Sanchez and N. P. Dasgupta (University of Michigan, Ann Arbor, USA), the goal of this work was to suppress dendrites by high surface area deposition of lithium metal. Carbonised electrospun polyacrylonitrile was shown as an example of a three-dimensional (3D) current collector concept from prior literature (17). In this work, copper pillars were grown by electrodeposition *via* polycarbonate

membrane masking with pillars of differential sizes. 10  $\mu\text{m}$  pillars with 25  $\mu\text{m}$  spacing showed an improvement in residual dead lithium however 2  $\mu\text{m}$  pillars with 5  $\mu\text{m}$  spacing gave a compact layer. At 0.2  $\mu\text{m}$  pillars with 0.5  $\mu\text{m}$  spacing there was very non-uniform surface lithium plating with a large amount of residual lithium when stripped. Cycling data showed up to double the lifetime for the 2  $\mu\text{m}$  pillars compared to flat copper. Further work investigated lithiophilic coatings to reduce the nucleation barrier. The first example chosen was ALD zinc oxide (ZnO) coating on flat copper which exhibited a smoother surface after lithium stripping. The same coatings were applied to 2  $\mu\text{m}$  and 0.2  $\mu\text{m}$  pillared samples. The cycle life for the 2  $\mu\text{m}$  sample was extended to triple that of the flat copper foil. With 10  $\mu\text{m}$  long and 2  $\mu\text{m}$  diameter pillars the CE of 99.3% was retained when cycled to 2 mAh. Data on the results from 0.2  $\mu\text{m}$  was not provided. X-ray photoelectron spectroscopy (XPS) results showed that all of the lithium was plated on top and the zinc was kept at the copper surface. In a following presentation from Dalhousie University (Canada), zinc was also successfully used to reduce the lithium plating nucleation barrier, down-selected from a wide range of other metals, with gold having been the only better option found.

'Electrolyte Studies Centred Around a Substituted Lithium Cobalt Phosphate Cathode Material' by S. A. Delp, J. L. Allen and T. R. Jow (US Army Research Laboratory, USA) showed data demonstrating that vinyl carbonate is not an option for high voltage cathodes due to poor oxidative stability. Various options were identified for discussion such as lithium difluoro(oxalato) borate (LiDFOB); tris(trimethylsilyl)borate (TMSB); tris(trimethylsilyl) phosphate (TMSP); fluoroethylene carbonate (FEC); and 1,1,1,3,3,3-hexafluoro-2-propanol (HFPIP). LiDFOB was confirmed to react on both electrode surfaces as well as most of the other compounds. Interestingly, lithium hexafluorophosphate ( $\text{LiPF}_6$ ) was found to help passivate the anode to mitigate continuous electrolyte decomposition. The passivating effect did not exist in the presence of some of the additives. Upon full charge cycle and lifetime analysis, TMSB was found to enable the most stable charge profile and CE.

## Solid State Ionic Materials

'Safe, High-Energy-Density, Solid-State Li Batteries' by E. D. Wachsman (Maryland Energy Innovation Institute, USA) used aluminium ALD coating to prevent lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) formation by

having formed lithium aluminate which was wetted well with lithium metal. Silicon partially coated on a pellet showed spontaneous wetting with contact on liquid lithium (18). Also, two other ALD coatings were shown to work.  $\text{Li}_2\text{MMn}_3\text{O}_8$  was used as the cathode material for samples manufactured using a solid oxide fuel cell tape-casting method. The work is currently being scaled from coin cell to 30  $\text{cm}^2$  cell. 10  $\text{mA cm}^{-2}$  cycling was recently achieved and it was demonstrated that operational cell failure can occur if the cell is driven beyond the lithium loading limit. The US Department of Energy (DOE) Advanced Research Projects Agency-Energy (ARPA-E) Integration and Optimization of Novel Ion-Conducting Solids (IONICS) programme and the DOE Vehicle Technologies Office (VTO) fast-charge programme goals for current density were achieved in this work. 100% CE was demonstrated over 480 cycles. A new line of research is now investigating Li-sulfur. Sulfur loading has been increased from 1  $\text{mg cm}^{-2}$  to 8  $\text{mg cm}^{-2}$  with 100% CE over 300 cycles with 700  $\text{mAh g}^{-1}$  capacity. A pouch cell was demonstrated to continue to operate after having been cut in half and left exposed to air. The modal pore size of the  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) porous anode is 5  $\mu\text{m}$  and 50–60% porous. 70% porosity was achievable by tape casting. 3D printing has enabled up to 85% porosity. Maintaining flatness during the scaling process is currently being investigated.

'Chemical and Electrochemical Stability of Fast Lithium Ion Conducting Garnet-Type Metal Oxides in  $\text{H}_2\text{O}$ , Aqueous Solution,  $\text{CO}_2$ , Li and S' by V. Thangadurai (University of Calgary, Canada) discussed the drive to move away from  $\text{LiLaTiO}_x$  due to the lithium instability of the titanium. Initially niobium and tantalum were utilised, subsequently materials utilised substitutions of scandium, yttrium, indium or full replacement such as zirconium, tin, hafnium. For LLZO further substitutions were investigated. Increasing octahedral sites in this structure drive lithium ion conductivity. However, there is a lower activation energy profile for conductivity through the route of octahedral  $\rightarrow$  tetrahedral  $\rightarrow$  octahedral as compared to conduction through purely octahedral sites. Safety and stability in the presence of water, carbon dioxide and sulfur have been studied in detail (19). These materials can either rapidly or very slowly degrade in water depending on the B site metals. Proton transport evidence has been observed however further work is still necessary to understand the physics (20).  $\text{Li}_{6.5}\text{La}_{2.5}\text{Ba}_{0.5}\text{ZrTaO}_{12}$  (LLBTZ) was shown to increase in conductivity

after exposure to water. Exposure to CO<sub>2</sub> forms Li<sub>2</sub>CO<sub>3</sub> in all garnet materials. Garnets were shown to be stable in the presence of sulfur (21). A wet solution method for ZnO coating using surfactants was exhibited which has provided similar results for lithium metal wettability as ZnO by ALD (22).

'First-Principles Models of Phenomena at Li-Metal/Anti-Perovskite Li<sub>3</sub>OCl Solid Electrolyte Interfaces' by K. Kim and D. J. Siegel (University of Michigan, Ann Arbor, USA) used density functional theory (DFT) work to predict a 6.39 electron volt (eV) bandgap. SEM data suggests that lithium metal wets the surface and is stable in contact with Li<sub>3</sub>OCl. Bulk structures were modelled via Murnaghan equation of state. Gibbs free energy and chemical potential were calculated at 300 K and 1 atmosphere. Six surface models were used and the (100) plane appeared the most stable and the lithium metal (100) plane matches it well. The oxygen terminated sites have a calculated contact angle of 52.6 degrees whereas the chlorine terminated sites had a contact angle above 120 degrees. Interfacial interactions narrow the electrochemical window by 2 eV. Consequently, lithium metal does not reduce Li<sub>3</sub>OCl though it is unstable with respect to many cathode materials.

## Conclusions

Interesting electrochemical analysis modelling and first principles modelling work was exhibited, some of which has been provided as open-source tools or will be soon provided. Key battery themes that were attended included lithium metal anodes, solid state conductive materials, interface engineering and electrolyte additives for stability. In relation to lithium metal anodes, there has been a surge of 'anode free' research and some consolidated understanding of lithium dendrite formation and control. Solid state conductor battery related sessions exhibited modelling work illustrating mechanistic detail for different materials. Interface engineering discussions included ALD coatings, mechanofusion and chemical routes to coatings. Electrolyte additives were well discussed by US Army Research Laboratory representatives amongst others, mainly focused on wholly fluorinated solvents or additives for good SEI stability and optimised overcharge protection.

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## The Reviewer



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