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Oxford Battery Modelling Symposium

Highlights of the latest developments in battery modelling: from atomistic length-scale to control modelling

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Introduction

The Oxford Battery Modelling Symposium was held in Oxford, UK, from 18th to 19th March 2019. The conference was specifically designed to gather mathematicians, chemists and engineers within the battery modelling community. It was very well received and brought together 170 participants with worldwide representation from academia, research organisations and industry involved in modelling at different scales (atomic length-scale, continuum and control-oriented modelling). This review will focus on eleven talks presented in the four sessions and organised as follows:

- Atomistic to continuum modelling
- Continuum modelling
- Continuum to control modelling
- Control-oriented modelling.

Atomistic to Continuum Modelling

Electrochemical processes can be modelled using a continuum approach (that relies on material specific parameters, sometimes difficult to measure) or from first principles. As electrochemical processes are thermally activated, in 'Connecting Electronic Structure to Phenomenological Continuum Models of Electrochemical Processes' by Anton Van der Ven (University of California Santa Barbara, USA) it was shown that temperature and entropy play a key role for understanding the physics and the properties of materials. As such, a statistical mechanics approach is beneficial, although computationally very demanding. Van der Ven introduced the open-source software Cluster Approach to Statistical Mechanics (CASM) developed in his group and available from GitHub (1). In CASM, for a certain material, the thermodynamic and kinetic properties obtained from density functional theory can be fed into continuum models to realise fast and computationally undemanding first-principle multiscale simulations for dynamic processes such as electrochemical processes. This tool can be used to predict thermodynamic and kinetic properties of various classes of materials (such as layered, olivines, spinels and alloys), see **Figure 1** (2).

In literature both accurate first-principle methods and continuum theories are available to predict the properties of materials and interfaces. However, rigorous ways to connect the two approaches are still lacking. In 'Mind the Gap – Towards an Atomistic Understanding of Battery Materials Interfaces', Denis Kramer (University of Southampton, UK) described strategies to build continuum models starting from first principle calculations and their application to crystallisation. The coverage effect in the size-stabilisation of nanocrystals during electrochemical processes and the crystallisation process of manganese(IV) oxide polymorphs have been discussed (3). Finally the effect of Li^+ ions in the stabilisation of some MnO_2 polymorphs was described in this framework.

In 'Modeling Porous Intercalation Electrodes with Continuum Thermodynamics and Multi-scale Asymptotics' by Manuel Landstorfer (Weierstrass Institute for Applied Analysis and Stochastics, Germany), a description of the procedure for modelling porous cathodes was provided. For such electrodes three scales can be identified (the double layer scale, the macroscopic porous media scale and the microstructure scale). Landstorfer started

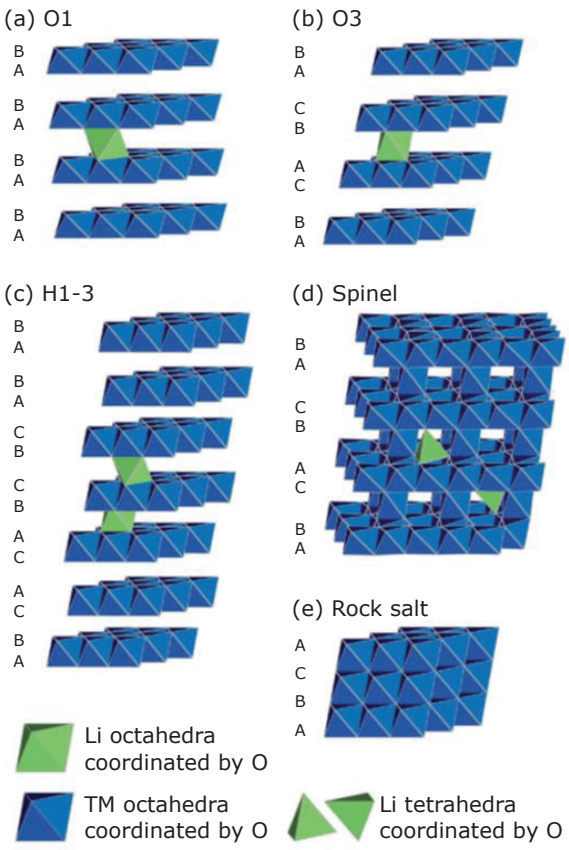

Fig. 1. Crystal structures relevant for layered Li intercalation electrodes. Blue octahedra represent MO_6 units and green octahedra/tetrahedra represent Li sites. (Reprinted with permission from (2). Copyright 2019 John Wiley and Sons)

by describing the metal-electrolyte interface and electron transfer in the double layer through a non-equilibrium thermodynamic continuum model (4). The model was scaled up to electrode particle scale and treated with a matched asymptotic expansion method. Finally, Landstorfer discussed a third scale: the macroscopic porous media scale. He introduced homogenisation techniques for the prediction of transport properties at porous scale. This multiscale methodology was applied to model thermodynamic properties, diffusion processes and the open circuit potentials of intercalation cathodes for Li-ion batteries with different chemical composition and porosity.

Continuum Modelling

'Electrochemical Energy Storage' by John Newman (University of California Berkley, USA) was a keynote lecture on mathematical modelling approaches for the design of batteries. Newman introduced various methodologies (such as continuum modelling, (kinetic) Monte Carlo and molecular dynamics) and their application to the modelling of intercalation electrodes and electrolytes in Li-ion batteries. He showed how these tools can improve understanding of the electrochemical processes as well as of failure mechanisms taking place in battery materials, helping to design high power and high energy battery materials.

Bob McMeeking (University of California Santa Barbara, USA) presented a model for the redox kinetics at an interface between a solid electrolyte and a Li metal anode in 'Redox Kinetics, Interface Roughening and Solid Electrolyte Cracking in Solid State Lithium-Ion Batteries'. This model was based on the extension of the Butler-Volmer equation through the inclusion of the effect of the mechanical stress across the anode-electrolyte interface. This method was applied to the investigation of the morphological stability of the interface between the Li anode and the solid electrolyte for various current densities and solid electrolyte resistivities. Moreover, the extended Butler-Volmer equation was used to model the evolution of cracking in ceramic solid electrolytes caused by Li insertion into pre-existing defects on the electrolyte surface. The model showed how the pressure generated by Li insertion into the flaw causes the propagation of cracking in the solid electrolyte and consequent Li dendrite growth. Finally, the extended Butler-Volmer equation was used to identify the maximum Li pressure and critical lengths (a_1) of defects within a series of ceramic electrolytes to avoid the propagation of Li dendrites (a_1 = 2 μm for $Li_7La_3Zr_2O_{12}$ (LLZO)) (5).

Continuum to Control Modelling

The kinetics and uniformity of Li insertion reactions at the solid-liquid interface govern the rate capability and lifetime of Li-ion batteries. Martin Bazant (Massachusetts Institute of Technology, USA) presented a model for the prediction of phase transformations of intercalation materials in 'Control of Battery Phase Transformations by Electro-Autocatalysis'. The approach was based on a thermodynamic framework for chemical kinetics applied to charge transfer (namely, the Marcus and extended Butler-Volmer equations) (6).

Reaction-driven phase transformations are common in electrochemistry, when charge transfer is accompanied by ion intercalation or deposition in a solid phase. The model allows rationalisation

of phase separation of Li-rich and Li-poor islands for low discharge rates that affect the stability and cyclability of Li-ion batteries. The model also proved that high discharge rates favour the formation of solid-solution phases through an electro-autocatalytic mechanism, later experimentally confirmed for lithium iron phosphate (LFP) (7). The model can be extended to the investigation of electrodeposition, corrosion, chemical intercalation, precipitation and cell biology.

Göran Lindbergh (KTH Royal Institute of Technology, Sweden) presented an extended physics-based porous electrode model accounting for particle surface stress that was used to describe ageing of nickel manganese cobalt oxide cathode ($LiNi_xMn_yCo_zO_2$, NMC) with composition $x = y = z = 0.33$ (namely NMC111). In 'An Extended Porous Electrode Model for NMC111 in Lithium-Ion Batteries' the performances of NMC111 were experimentally investigated *via* a galvanostatic intermittent titration technique and two models were used to fit the experiments: (i) a standard pseudo-two-dimensional (P2D) model; and (ii) an extended surface stress P2D model that included a stress factor depending on the Li concentration gradient in the material. Model (ii) could accurately extract transport, kinetic, thermodynamic and stress properties for the whole spectrum of operative conditions (low and high charge-discharge rates, temperature and external pressure). Although the standard model works well for low potentials (less particle surface stress), the porous electrode stress model predicts the ageing of NMC at high potentials (high surface stress).

'Physically-Informed Models for Improved Cell Design and Operation of Lithium-Sulphur Cells' by Monica Marinescu (Imperial College London, UK) was a lecture about the necessity of using physically-informed models to predict the mechanisms and performance of batteries. The accumulated experience on physically-informed models for Li-ion was used as a starting point for engineering Li-S batteries. Modified equivalent circuit network models were used for Li-S batteries modelling in order to take into account phenomena like shuttling, dissolution and precipitation. Moreover, simple physics-derived zero-dimensional (0D) and one-dimensional (1D) continuum models for the prediction of open circuit voltage and of the effects of mass transport on discharge, degradation mechanisms and capacity fade for commercially-sized Li-S batteries were presented (8–10).

Control-Oriented Modelling

Gregory Plett (University of Colorado, Colorado Springs, USA) delivered a keynote lecture titled 'Physics-Based Reduced-Order Models of Lithium-Ion Cells for Battery Management Systems' about physically-informed control models. Plett reviewed the standard physics-based model particularly focusing on how this model could be converted to a physics-based reduced-order model (PBROM). Battery-management systems provide a continuous estimate of state-of-charge, state-of-health, available energy and available power of battery packs. Traditional computational methods rely on empirical equivalent circuit models of the batteries. These models are computationally fast and robust. However, although accurate for many tasks, they cannot predict the internal electrochemical state of the cell. On the other hand, physics-based models that provide good predictions of the internal electrochemical state are too complex to apply to battery-management systems, which are heavily parametrised and have robustness and convergence issues. PBROM is a method that, while reducing the computational requirement of physics-based models, retains their prediction accuracy and can be used for battery management systems.

In 'Decoding the Electron Swelling for Advanced Battery Diagnostics' Anna Stefanopoulou (University of Michigan, USA) presented a conjugated experimental and computational control model to account for battery degradation. Since standard control models do not account for swelling and ageing, during the talk Stefanopoulou introduced experimental apparatus to probe battery degradation and convert the observables (measured terminal voltage and surface temperatures) into parameters to implement control models to predict swelling and ageing (11). In particular, observations of the cell swelling during charging were used to estimate the loss of active material and loss of Li inventory in the anode, which is useful for avoiding Li-plating during fast charge.

The last talk was delivered by Scott Trimboli (University of Colorado, Colorado Springs, USA). The 'Model Predictive Control using Physics-Based Models for Advanced Battery Management' was a lecture on the model predictive control (MPC) developed in collaboration with Plett. Starting from the PBROM, Trimboli showed the mathematical implementation of MPC. MPC is an effective real-time control strategy that employs a 'look-ahead' approach to foresee dynamic behaviours in

the battery pack before they happen. This approach can be coupled with the ability of PBROM to enforce hard constraints on internal electrochemical variables (precursors to degradation or unsafe operation conditions), making MPC appealing for advanced battery management, where safety, lifetime and improved performance are crucial (12).

Conclusions

The Oxford Battery Modelling Symposium aimed to bring together the battery modelling community. It was well attended and the 12 talks as well as the 25 posters were high quality. The four sessions of talks were successfully organised to provide a full overview of the current state of the art in Li-ion and next generation battery modelling, spanning from first-principle investigations to control-oriented approaches.

References

1. 'CASM: A Clusters Approach to Statistical Mechanics', prisms-centre, GitHub: https://github.com/prisms-center/CASMcode (Accessed on 2nd September 2019)
2. M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng and A. Van der Ven, *Adv. Energy Mater.*, 2017, **7**, (20), 1602888
3. W. Sun, D. A. Kitchaev, D. Kramer and C. Ceder, *Nature Commun.*, 2019, **10**, 573
4. M. Landstorfer, C. Guhlke and W. Dreyer, *Electrochim. Acta*, 2016, **201**, 187
5. R. M. McMeeking, M. Ganser, M. Klinsmann and F. E. Hildebrand, *J. Electrochem. Soc.*, 2019, **166**, (6), A984
6. M. Z. Bazant, *Faraday Discuss.*, 2017, **199**, 423
7. J. Lim, Y. Li, D. H. Alsem, H. So, S. C. Lee, P. Bai, D. A. Cogswell, X. Liu, N. Jin, Y. Yu, N. J. Salmon, D. A. Shapiro, M. Z. Bazant, T. Tyliszczak and W. C. Chueh, *Science*, 2016, **353**, (6299), 566
8. T. Zhang, M. Marinescu, S. Walus and G. J. Offer, *Electrochim. Acta*, 2016, **219**, 502
9. T. Zhang, M. Marinescu, S. Walus, P. Kovacik and G. J. Offer, *J. Electrochem. Soc.*, 2018, **165**, (1), A6001
10. M. Marinescu, L. O'Neill, T. Zhang, S. Walus, T. E. Wilson and G. J. Offer, *J. Electrochem. Soc.*, 2018, **165**, (1), A6107
11. K.-Y. Oh, J. B. Siegel, L. Secondo, S. U. Kim, N. A. Samad, J. Qin, D. Anderson, K. Garikipati, A. Knobloch, B. I. Epureanu, C. W. Monroe and A. Stefanopoulou, *J. Power Sources*, 2014, **267**, 197
12. M. S. Trimboli, G. L. Plett, R. A. Zane, K. Smith, D. Maksimovic, M. Evzelman, D. Costinett and R. D. Anderson, Utah State University, 'Model Predictive Control and Optimization for Battery Charging and Discharging', *US Patent Appl.* 2016/0,336,765

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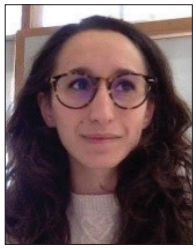

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