Multi-Temperature *In Situ* Magnetic Resonance Imaging of Polarization and Salt Precipitation in Li-Ion Battery Electrolytes

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The parameterization and validation of robust electrochemical models for lithium-ion batteries in automotive applications, which are intended to address both the state of charge (SOC) and state of health (SOH) estimation problems, is an important milestone in their widespread deployment. A significant fraction of overall polarization stems from concentration gradients that form in the electrolyte domain and their attendant effect on the mass transport parameters, which have recently been shown by *in situ* MRI to be quite significant, even within modest operational regimes.[1] The effect of temperature on these concentration gradients remains to be explored by *in situ* MRI.

The mass transport in the electrolyte domain is governed by competing diffusion and migration fluxes of the salt ions, which can produce a steady-state condition under constant-current cycling (see Figure 1A). Using *in situ* MRI, the evolution of this gradient toward the steady-state upon constant-current charging can be monitored under a range of temperature conditions.[2] A surprising outcome of these studies was that at 10°C, an equal parts (v/v) mixture of EC/DEC with 1.00 M $LiPF_6$ exhibited salt precipitation (Figure 1B) with a current density corresponding to 6 $A{\cdot}m^{-2}$ (or ~C/3), whereas the same mixture and cell construction could be polarized without difficulty at room temperature.

An electrolyte composition with better low-temperature characteristics, 1.00 M $LiPF_6$ in EC/PC/DMC, 5:2:3 (v/v), was successfully polarized with the same 6 $A{\cdot}m^{-2}$ current density, and a significant effect on gradient magnitude is measured with decreasing temperature. Previous *ex situ* experiments[3] were used to compare the nearly uniform concentration gradient in the centre of the cell with the predicted value from the model. In this region, the inter-electrode spacing should play no role in determining the steady-state concentration gradient, which was borne out within 3σ confidence intervals and confirms that the *in situ* MRI technique can generate steady-state transport parameters relevant to real battery modelling efforts.

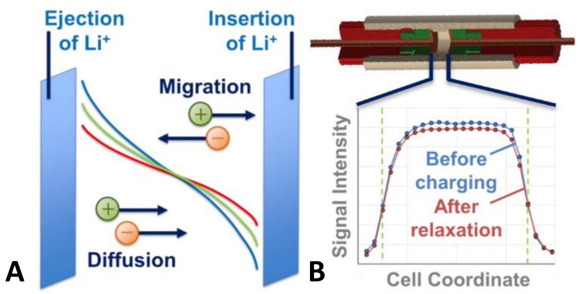

Figure 1 – A) Model schematic illustrating concentration gradient formation and the effect of temperature; B) *in situ* cell design and demonstration of salt precipitation at low temperature.

References

[1] Krachkovskiy, S. A.; Bazak, J. D.; Werhun, P.; Balcom, B. J.; Halalay, I. C.; Goward, G. R.. *J. Am. Chem. Soc.* **2016**, *138* (25), 7992–7999.

[2] Bazak, J. D.; Krachkovskiy, S. A.; Goward, G. R. *J. Phys. Chem. C*, **2017**, *121*, 20704-20713.

[3] Krachkovskiy, S. A.; Bazak, J. D.; Fraser, S.; Halalay, I. C.; Goward, G. R. *J. Electrochem. Soc.* **2017**, *164* (4), A912–A916.