

In Operando Visualization of Sodium Battery Chemistry by Magnetic Resonance Imaging

Joshua M. Bray¹, Galina E. Pavlovskaya², Claire L. Doswell¹, Heather Au³, Hande Alptekin³, Maria-Magdalena Titirici³, Thomas Meersmann², Melanie M. Britton¹

¹ School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK. ² Sir Peter Mansfield Imaging Centre, School of Medicine, University of Nottingham, Nottingham, NG7 2RD, UK. ³ Department of Chemical Engineering, Imperial College, Kensington, London, SW7 2AZ, UK

Introduction: In recent years, there has been increasing interest in sodium ion batteries (SIBs) as a promising alternative to lithium ion batteries (LIBs). In particular, SIBs offer advantages in cost and sustainability over current LIBs, while still providing high energy density. However, despite increased research intensity, SIBs still face significant challenges preventing their commercialisation, which is driving the development of new SIB materials. In parallel with the demand for new SIB materials, there is an equal demand for new *operando* analytical techniques [1-3] to facilitate the identification of optimised electrolytes and electrode materials, and fundamental understanding of the factors controlling the composition and stability of the solid-electrolyte interphase (SEI) and the formation of dendrites. ²³Na MRI offers a valuable opportunity by which SIBs can be investigated and optimised, as it is possible to visualise the structure and distribution of the electroactive species directly. *In operando* ¹H and ²³Na nuclear magnetic resonance (NMR) spectroscopy and imaging (MRI) experiments are reported, which identify Na species and map their distribution in the electrode and electrolyte during charge cycling and galvanostatic plating.

Experimental: ¹H and ²³Na NMR imaging, combined with ²³Na NMR spectroscopy, were performed, during galvanostatic cycling and plating in a model sodium-ion battery comprising sodium metal and amorphous carbon electrodes with a 1 M sodium hexafluorophosphate in 1:1 ethylene carbonate:dimethyl carbonate electrolyte.

Results and Discussion *In operando* ²³Na nuclear magnetic resonance (NMR) spectroscopy and imaging (MRI) experiments enabled the identification of Na species and map their distribution in the electrode and electrolyte during charge cycling and galvanostatic plating [4]. The formation and evolution of sodium dendrites were observed by ²³Na NMR spectroscopy and MRI and the formation, growth and microstructure of these dendrites were visualised by three-dimensional (3D) ¹H MRI of the electrolyte.

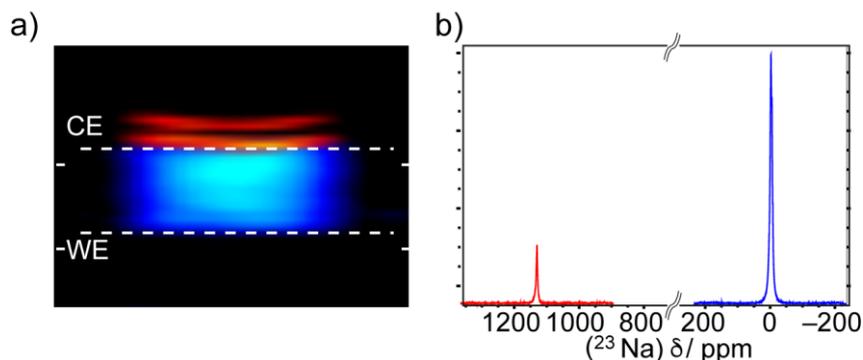


Fig. 1a) 2D ²³Na MRI of sodium in Na metal (red) counter electrode (CE) and electrolyte (blue). The position of the CE and carbon working electrode (WE) are indicated with dashed lines. b) ²³Na NMR spectra for Na in the electrolyte (blue) and Na metal electrode (red).

Conclusions: ¹H and ²³Na MRI has the potential to provide a step change in understanding of performance and failure mechanisms in SIBs.

References: [1] Britton *Prog. Nucl. Magn. Reson. Spec.* **101** (2017) 51 [2] Britton, et al. *J. Phys. Chem. Lett.* **4** (2013) 3019 [3] Bray et al. *Angew. Chem.* **55** (2016) 9394 [4] Bray et al. *under revision*.