

Multifunctional Materials: a Promising Approach for Improving the Durability and Performance of Li-Ion Batteries

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Parasitic reactions involving acid species are a main cause for performance degradation in Li-ion batteries (LIBs) with LiPF₆ electrolyte solutions, regardless whether they involve or not Mn dissolution. We present our recent progress in the understanding of Mn species in LIBs¹ and on two mitigation measures for degradation reactions,² namely chelation of dissolved transition metal (TM) ions and scavenging of acid species, improved by the use of multifunctional materials (MFMs) in separators³ and binders.⁴ Multifunctional separators (MFSs) were the primary test platform during the first phase of our work, due to the ease of analysis and clarity in interpretation they offer for cell components' characterization. MFSs can trap Mn cations, scavenge HF and/or disperse alkali metal ions, with significant benefits for LIB performance: increased capacity retention during cycling at room and high temperatures, also improved rate performance. Cells having LiMn₂O₄, LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ or LiNi_{0.5}Mn_{1.5}O₄ cathodes, graphite anodes, and LiPF₆/carbonates solutions underwent galvanostatic cycling and electrochemical ac impedance (EIS) measurements. Harvested cell components were analyzed by XRD, ICP-OES, XANES, HR-TEM, SEM-EELS, FIB-SEM, and MAS-NMR. In LIBs with cathodes affected by Mn dissolution, cell performance improvements are enabled by trapping of Mn ions in the MFS and reduced deposition at anodes. After 55°C cycling for 12 weeks, the electrode-electrolyte interface and ion-transfer resistances of anodes and cathodes in LiMn₂O₄-graphite cells are ~3x smaller in cells with MFSs than in cells with polypropylene separators; moreover, the interfacial resistances of electrodes from cells with MFSs are smaller than the corresponding resistances in baseline cells after 1 week of cycling. The EIS results are corroborated by FIB-SEM data showing a ~2.6x smaller average SEI thickness on the graphite electrode from a cell with a MFS than from a cell with a baseline separator. We show that saturation of MFSs with Mn ions does not increase the capacity fade rate. Furthermore, MFSs prevent Mn deposition on graphite during cell formation, suggesting that creation of a “sound” SEI is a prerequisite for improved LIB performance. EDX analysis of the SEI shows differing F:P ratios in graphite electrodes from cells with MFSs vs. propylene separators, while ¹⁹F MAS-NMR data show 5 times more LiF deposited in MFSs than in plain separators from LiMn₂O₄-graphite cells, indicative of qualitative differences in the SEIs. The benefits from MFSs extend to cell chemistries not affected by TM dissolution, like LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂-graphite cells. Finally, we will demonstrate that MFMs improve the cycling performance of LiNi_{0.5}Mn_{1.5}O₄-graphite cells and also present results on the benefits for LIB performance from novel multifunctional binders.

References:

[1] Z. Li et al. *J. Power. Sources* **272** (2014) 1134; Y. Shilina et al. *Anal. Chem.* **88** (2016) 4440; A. Banerjee et al. *J. Am. Chem. Soc.* **139** (2017) 1738. [2] G. Amatucci et al. *Electrochim. Acta* **45** (1999) 255. [3] A. Banerjee et al. *ACS Energy Lett.* **2** (2017) 2388; A. Banerjee et al. *J. Power Sources* **341** (2017) 457; A. Banerjee et al. *Electrochem. Soc.* **164** (2017) A6315; A. Banerjee et al., *J. Electrochem. Soc.* **163** (2016) A1083; A. Banerjee et al. *Adv. Energy Mater.* **7** (2016) # 1601556. [4] N.P.W. Pieczonka et al. *Adv. Energy Mater.* **5** (2015) # 1501008.