**Probing Redox Reactions in Rechargeable Batteries by *Operando* Electron Paramagnetic** **Resonance**

Tang, M., Li, X. (FSU, Chemistry); Dalzini, A., Song, L. (NHMFL) and Hu, Y.-Y. (FSU, Chemistry and NHMFL)

**Introduction**

 To further improve the frontier of designing high-energy cathode materials, new chemistry is needed to enable additional capacity beyond what transition metal (TM) redox can offer. The combination of TM with oxygen (O) redox can lead to synergy for providing extra capacity harvested from both TM and O redox reactions. Electron paramagnetic resonance (EPR) is sensitive to study the unpaired/delocalized electrons of TM and O. Lithium rich samples such as Li1.2Ni0.2Mn0.5O2 (LNMO) show additional capacity due to electron hole formation or O2 release, which is strongly dependent on the stability of the oxygen atom local environments. *Operando* EPR is a powerful tool to determine the redox evolution of both TM and O upon cycling.1

**Experimental**

The synthesized LNMO was mixed with polyvinylidene fluoride and conductive carbon. The mixture was dispersed in NMP and manually grinded in an agate mortar. The mixture was put onto Ti mesh and dried at 120 °C for 4 hours under vacuum before assembly in argon filled glove box. The LNMO and Li metal electrodes were separated by one piece of porous glass microfiber. The whole content of the battery was soaked in the LP30 electrolyte. The assembled bag cell was positioned in the center of EPR cavity. CW-EPR spectra under kinetics mode were recorded while cycling the battery. Simulation and integration were performed by home-developed MatLab scripts. High-frequency and -field EPR spectra were recorded on a homebuilt spectrometer at the EPR facility of NHMFL (Tallahassee, FL). The instrument is a transmission-type setup in which microwaves are propagated in cylindrical light pipes. A superconducting magnet (Oxford Instruments) capable of　reaching a field of 17 T was employed.2

**Fig.1** Electrode structure with the relationship of EPR spectrum. The bottom is the EPR integral evolution of Mn4+ within LMNO//Li half battery.

**Results and Discussion**

*Operando* EPR signal on LNMO shows a bilinear decrease for the Ni2+→Ni3+→Ni4+ two-step oxidation at the early stage of the 1st charge (step 1 and 2 in **Fig.1**). The decrease slows down at 4.0 V partially due to the reversible O2-→O2n- oxidation. The relatively flat increase in the EPR signal at the beginning of 1st discharge is a result of competition between O reduction causing a decrease in the EPR signal and Ni reduction leading to an increase in the EPR signal. Once the O reduction process ceases, the increase of the EPR signal is faster as a result of Ni3+→Ni2+ reduction. Below 3.0 V, Mn4+→Mn3+ reduction takes place, resulting in the drop of the Mn4+ EPR signal.1 In addition, *operando* EPR was first employed to determine the Na microstructures.2 Well-resolved EPR spectra with axial configuration obtained at 319 GHz show more featured fine structure, which was obscured in X-band EPR (**Fig.2**).2

**Conclusions**

**Fig.2** CW-EPR spectra of LMO cathodes recorded at a) X-band and room temperature and b) 319 GHz and 5 K.

 The capability of *operando* EPR indirectly probing changes associated with Mn4+ and indirectly detecting variations in Ni and O based on their couplings to Mn4+ allows the disentanglement of the complex puzzle.

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**References**

[1] Tang, M., *et al.*, J. Phys. Chem. Lett., **8**, 4009–4016 (2017).

[2] Tang, M., *et al.*, in preparation.