In-situ Paramagnetic ^{17}O NMR Studies on High-Voltage Cathodes

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Introduction

Rechargeable Li-ion batteries (LIBs) as the leading energy-storage technology have attracted great research efforts. [1] Nuclear Magnetic Resonance (NMR) has been demonstrated as a suitable tool for determining Li local environments and their evolution during electrochemical operation. [2] O redox has been hypothesized to play an important role in increasing energy density of high-voltage cathodes. However, due to strong nuclear-electron dipolar interactions and extreme low natural abundance (0.037%) for NMR active ^{17}O, only a few reports exist for paramagnetic ^{17}O NMR. *In-situ* ^{17}O NMR can follow the O evolution during battery cycling to offer insights that cannot be obtained from *ex situ* studies. Even though the resolution of static *operando* NMR is poor for the paramagnetic cathode systems, it is sufficient to follow O evolution in real time.

Experimental

Plastic bag cell batteries were assembled in an argon-filled glove-box and placed inside a home-built static NMR probe. ^{17}O NMR spectra were collected while the batteries were cycled at a rate of C/50, with the theoretical capacity C=458 mAh/g. All *operando* ^{17}O NMR acquisitions were carried out on a Bruker Avance I spectrometer in a 19.6 T magnetic field with a ^{17}O Larmor frequency of 112.57 MHz. The ^{17}O spectra were obtained using a qCPMG sequence with a 90° pulse length of 1.56 µs. qCPMG can effectively excite extremely broad paramagnetic ^{17}O spectra under static conditions. 18k transitions were accumulated for each spectrum with a recycle delay of 0.4 s. The transmission frequency (SFO1) was located at 2000 ppm. Spectra were analyzed by using Topspin (version 3.5) and Matlab (version R2014b). Matlab codes were developed to process and analyze qCPMG spectra.

Results and Discussion

Selective *operando* ^{17}O NMR spectra are shown in the Figure 1a for the first charge-discharge process. Clear evolution is observed for the ^{17}O spectra of Li$_2$MnO$_3$. It decreases upon charge and increases upon discharge (the top yellowish trend shown in Fig. 1(a)). Quantitative integration of ^{17}O NMR spectra collected upon the first two cycles as a function of capacity is shown in Figure 1(b). There is about 0.03 Li extracted at the beginning of the 1st charge with voltage below 4.4 V. This period is assigned to the oxidation of residual

Figure 1. *In-situ* paramagnetic ^{17}O NMR spectra(a) and quantification (b) on Li$_2$MnO$_3$ upon the first 2 cycles.

Mn^{3+}→Mn^{4+}. Linearly decreased signal is observed for O upon voltage above 4.4 V. This is mainly due to the formation of O^{2-} + e$^-$→O$_2^{n-}$. Li re-intercalation occurs upon discharge from 5.0 V to 4.0 V, electrons are injected into O species O$_2^{n-}$ + e$^-$→O^{2-}. Below 4.0 V, Mn^{4+} is reduced to Mn^{3+}, which shows less spin density transfer, resulting in increased integral at the end of discharge. At the beginning of the 2nd charging process, Mn^{3+} is first oxidized to Mn^{4+} at low voltage along with partial paramagnetic O$_2^{n-}$ formed, both cases weaken O signal in the range of 2.0~4.0 V. Further charge to 5.0 V, the high potential accelerates O$_2^{n-}$ formation along with O gas release. Because of the accumulated paramagnetic O$_2^{n-}$, the O signal is significantly weakened furthermore. The 2nd discharge resembles the trend from the 1st discharge.

Conclusions

Optimized *in-situ* ^{17}O paramagnetic NMR is implemented to monitor O redox in real time. We are able to quantify the amount of irreversible O loss (~10% in Li$_2$MnO$_3$ system) and O in participating reversible redox during cycling operation.

Acknowledgements

References

[1] Tarascon, J.-M., *et al.*, Nature, **414**, 359–367 (2001).
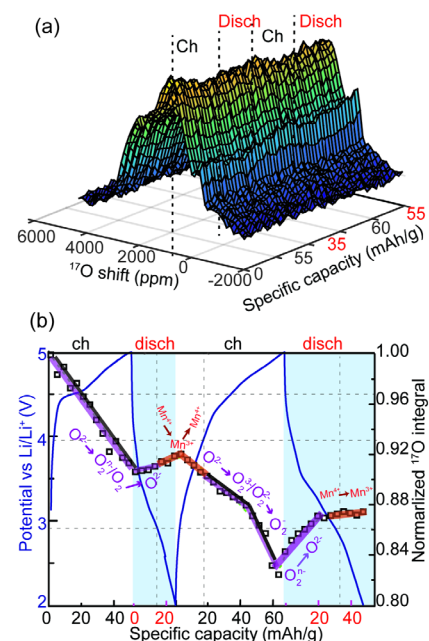[2] Grey, C. P., *et al.*, Chem. Rev., **104,** 4493–4512 (2004).