

Determination of Charge Distribution within Organic Electrode by *In Operando* EPR

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Introduction

Probing the distribution and dynamics of reactive electrons can help to understand the mechanism of electrode reactions and improve battery performance. Extensive efforts have been directed to understand the interaction and/or distribution of Li^+ and e^- into organic cores. Electron paramagnetic resonance (EPR) has been proven as a nondestructive and sensitive tool for investigating unpaired electron behaviors with both *ex situ*¹ and *in situ* experiments.² *In operando* EPR is for the first time employed to determine the states and distribution of electrons and Li^+ ions within 7,7,8,8-tetracyanoquinodimethane (TCNQ) electrode.³

Experimental

The active material TCNQ, binder PTFE, and acetylene black were mixed with a weight ratio of 60:30:10. Ethanol was chosen as mixing solvent during grinding in an agate mortar. The dried electrodes were transferred into an Argon-filled glove-box for battery assembly. The cathode LiCoO_2 (LCO, EPR silent) and anode TCNQ were separated by porous glass microfiber (Whatman, type GF/D), soaked with the LP30 electrolyte. The battery was electrochemically cycled inside an EPR cavity at a rate of C/15, with the set capacity of C=130 and 260 $\text{mAh}\cdot\text{g}^{-1}$ for LCO and TCNQ, respectively.

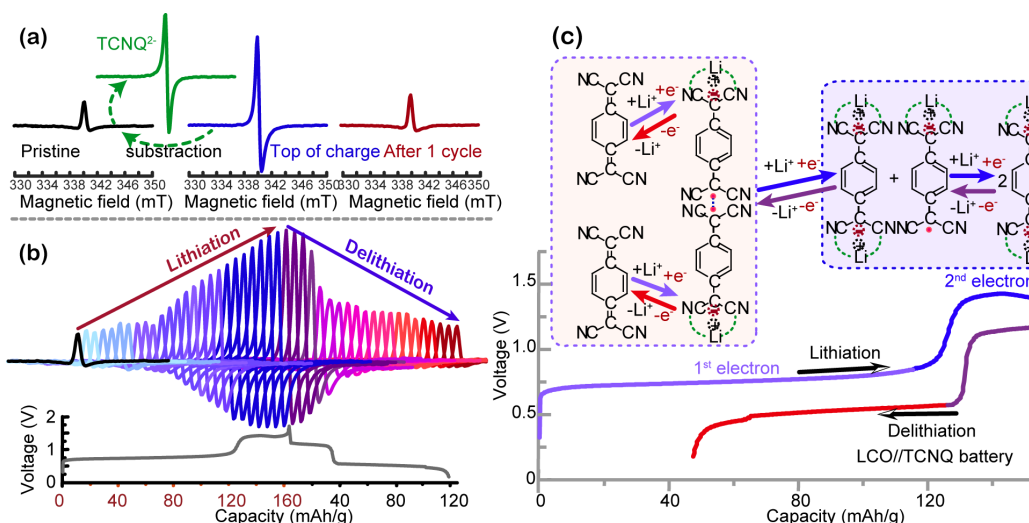


Fig.1 (a) and (b) *In operando* EPR spectra of a LCO//TCNQ bag-cell battery; (c) Proposed reaction mechanism for (d)lithiation of TCNQ electrode.

Results and Discussion

The pristine LCO//TCNQ battery shows an asymmetric EPR spectrum in **Fig.1a** and **1b**. At top of charge, increased signal is obtained with pure symmetric signal for TCNQ (simulated). Quantitative studies reveal that no radical formation during electrochemical cycling as demonstrated in **Fig.1c**. TCNQ dimer, other than electron delocalization or radical, is determined to be formed during the first electron injection upon lithiation; and followed by unpaired electron coupling to allow delocalization of electrons, which gives increased EPR signal during the 2nd electron injection.

Conclusions

Nondestructive *in operando* EPR has been performed on organic TCNQ electrode, which shows a two-electron reaction. The integrated EPR signal reflects the distribution of electron and Li^+ during each electrochemical cycling step. No radical is detected for organic TCNQ electrode.

Acknowledgements

This work was supported by the National Science Foundation under grant no. DMR-1508404. The EPR experiments were carried out at the National High Magnetic Field Laboratory, which is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida.

References

- [1] Botko, M., *et al.*, Acta Physica Polonica A, **126**, 252–253 (2014).
- [2] Tang, M., *et al.*, J. Phys. Chem. Lett., **8**, 4009–4016 (2017).
- [3] Hanyu, Y., *et al.*, Sci. Rep., **2**, 453 (2012).