

Radical Cation Stability vs. Redox Shuttle Performance in Lithium-Ion Batteries

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Redox shuttles are electrolyte additives that protect batteries from overcharge and balance charge among multiple batteries.¹ Redox shuttles based on 1,4-dimethoxybenzene,^{2,3} *N*-alkylphenothiazines,⁴ and TEMPO⁵ derivatives have been reported to protect certain lithium-ion batteries (LIBs) – often LTO/LiFePO₄ and graphite/LiFePO₄ – from overcharge for 100 or more cycles. Eventually these electrolyte additives fail to limit cell voltage, presumably due to decomposition in oxidized state, or radical cation version (for aromatic compounds), which are electron deficient and positively charged, making them especially reactive species.

In order to design redox shuttles with longer lifetimes and/or higher oxidation potentials, it would be beneficial to have a fast screening method to predict overcharge performance prior to assembling coin cell batteries. Screening dozens or hundreds of redox shuttle candidates could help narrow down the search for which compounds are worth testing. Here we wanted to determine if the stability of the radical cation form of reported redox shuttle additives could be used to predict overcharge performance, then, if successful, use the method to screen new candidates.

A variety of spectroscopic methods have been used to analyze aromatic radical cations including UV-vis-NIR spectroscopy and electron paramagnetic (EPR) spectroscopy. Both of these methods require dilute solutions (~10⁻³–10⁻⁴ M) of radical cation to ensure analysis of single molecules instead of aggregates, and to avoid saturating detectors. While EPR spectroscopy is more specific to radical species, it is time consuming and expensive instrument to purchase, so our goal was to use UV-vis spectroscopy for correlation and prediction of redox shuttle performance.

A variety of redox shuttle additives (**Figure 1**) were transformed into their radical cation forms using the chemical oxidant tris(2,4-dibromophenyl)aminium hexachloroantimonate, also known as Magic Green.⁶ Dichloromethane was used as a solvent due to its low cost and generally anhydrous nature.

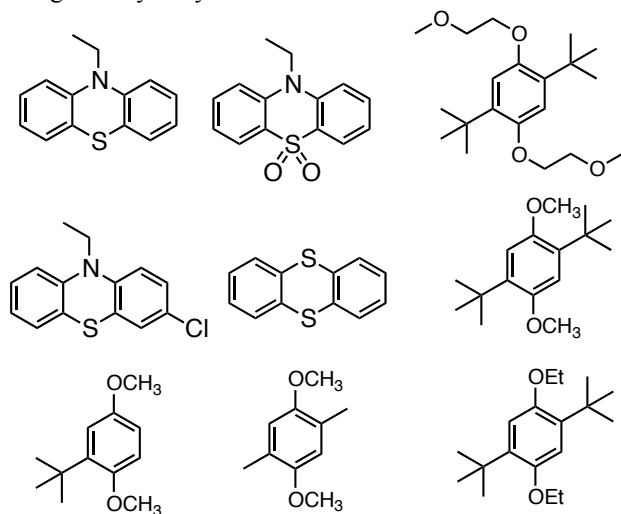


Figure 1. Examples of reported redox shuttle additives examined in this study.

UV-vis spectra of the radical cations were obtained and monitored over time. The faster the decay in peak intensity, the less stable the radical cation is. An example of a UV-vis spectrum plotted over time is shown in **Figure 2** in which the radical cation of a dimethoxybenzene decays rather rapidly in dichloromethane.

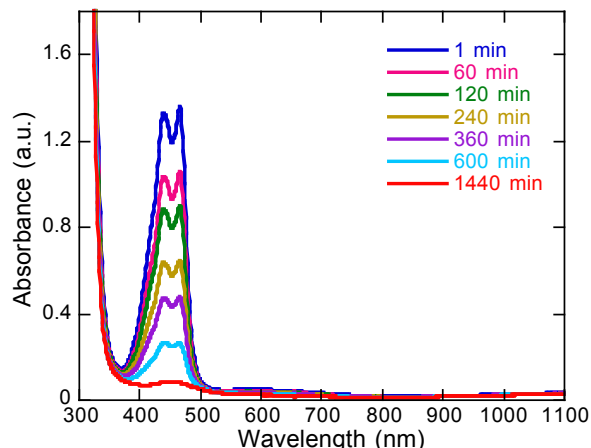


Figure 2. UV-vis. absorption spectrum over time of the radical cation of a 1,4-dimethoxybenzene derivative in dichloromethane.

When monitoring the rate of decay of the radical cations, one finds that the faster the rate of decay, generally the fewer number of overcharge cycles occur before additive failure. We also monitored decay of the intensity of EPR spectra of select radical cations, also generated by chemical oxidation, and found similar trends. This correlation between radical cation stability and number of overcharge cycles supports that radical cation decomposition leads to redox shuttle failure, and is furthermore interesting that a correlations exists despite concentration differences of two orders of magnitude and switching from a carbonate solvents with lithium salts (battery electrolyte) to dichloromethane. Our current work is focused on improving prediction reliability by optimizing conditions and testing new redox shuttle candidates.

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References

- (1) Wang, Q.; Zakeeruddin, S. M.; Exnar, I.; Grätzel, M. *Electrochem. Commun.* **2008**, *10*, 651.
- (2) Buhrmester, C.; Chen, J.; Jiang, J.; Wang, R. L.; Dahn, J. R. *J. Electrochem. Soc.* **2005**, *152*, A2390.
- (3) Zhang, L.; Zhang, Z.; Redfern, P. C.; Curtiss, L. A.; Amine, K. *Energy Environ. Sci.* **2012**, *5*, 8204.
- (4) Buhrmester, C.; Moshurchak, L. Wang, R. L.; Dahn, J. R. *J. Electrochem. Soc.* **2006**, *153*, A288.
- (5) Buhrmester, C.; Moshurchak, L. M.; Wang, R. L.; Dahn, J. R. *J. Electrochem. Soc.* **2006**, *153*, A1800.
- (6) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.