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## COMMUNICATION

## 3,7-Bis(trifluoromethyl)-*N*-ethylphenothiazine: A Redox Shuttle with Extensive Overcharge Protection in Lithium-Ion Batteries

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**3,7-Bis(trifluoromethyl)-*N*-ethylphenothiazine (BCF3EPT) was evaluated as a redox shuttle for overcharge protection in lithium-ion batteries. Constant-charging experiments were performed to compare the compound to 1,4-di-*tert*-butyl-2,5-dimethoxybenzene and *N*-ethylphenothiazine. BCF3EPT showed significantly longer overcharge protection when compared to either benchmark at the same concentrations in LiFePO<sub>4</sub>/graphite batteries.**

### Introduction

Overcharge occurs in lithium-ion batteries (LIBs) when cell potential rises above the battery's end-of-charge potential. Overcharge can occur if batteries connected in a series have different capacities; in this situation, lower-capacity batteries become fully charged before higher-capacity batteries are charged, and continued application of current causes the lower-capacity batteries to reach undesirably high potentials.<sup>1-4</sup> During overcharge, irreversible over-delithiation results in decreased lifetimes; oxidation of the electrolyte produces gases, causing increased internal pressure; and exothermic reactions raise battery temperatures, potentially leading to smoking, fires, and explosions.

One approach to prevent overcharge is to partially charge battery packs, but this practice limits the capacity available to users. An alternate approach is to incorporate redox shuttle additives into the battery electrolyte.<sup>5-7</sup> These additives serve as an internal shunt, shuttling excess current between battery electrodes by oxidizing at the cathode/electrolyte interface, then diffusing to the anode/electrolyte interface, where they are reduced to their neutral forms. While hundreds of compounds have been tested as redox shuttles, only a few have been reported to have extensive overcharge protection.<sup>8-16</sup>

Redox shuttle performance is usually reported in terms of the number of cycles for which battery voltage is controlled (limited) when charged to 200% of its normal charge capacity and then discharged. While this method of testing allows for an analysis of the retention of charge and discharge capacity during cycling, the batteries are only in overcharge ca. 33% of the time. Additionally, batteries are often cycled to voltages higher than their end-of-charge

potentials, which limits long-term battery capacity and results in a larger portion of charging time spent in overcharge during later cycles. An alternative method for evaluating overcharge performance is to apply constant charge, meaning that batteries spend the entire experiment – with the exception of the initial charging step – in overcharge, thereby eliminating 66% of testing time. Although this protocol does not allow for evaluation of battery capacities at each cycle, its efficiency makes it a beneficial alternate to charge/overcharge/discharge protocols, under which some batteries require a year or more to fail.

Recently we reported preliminary overcharge testing of 3,7-bis(trifluoromethyl)-*N*-ethylphenothiazine (BCF3EPT, Figure 1) in LiFePO<sub>4</sub>/graphite batteries as part of a series of related redox shuttle candidates using the commonly employed 200% charge per cycle protocol. One of the batteries containing BCF3EPT was still cycling at the time of publication<sup>17</sup> and since then survived a total of 242 cycles before failing.<sup>18</sup> After BCF3EPT showed such promise relative to other 3,7-disubstituted phenothiazine derivatives, we wanted to test this redox shuttle side-by-side with compounds reported to have extensive overcharge performance. In this communication, we report a comparison of constant-charging experiments using BCF3EPT and two commercially available redox shuttles: *N*-ethylphenothiazine (EPT)<sup>12,13</sup> and 1,4-di-*tert*-butyl-2,5-dimethoxybenzene (DBB) (Figure 1).<sup>9-11</sup> Our results also include cyclic voltammetry, calculations of diffusion coefficients, and stability measurements of the compounds in solution in their neutral and oxidized forms.

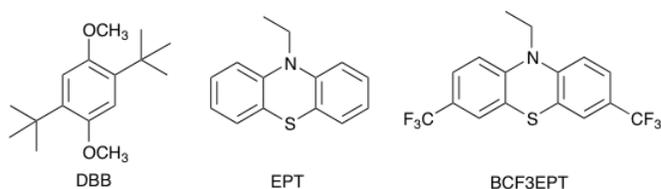


Figure 1. Representations of the chemical structures of 1,4-di-*tert*-butyl-2,5-dimethoxybenzene (DBB), *N*-ethylphenothiazine (EPT), and 3,7-bis(trifluoromethyl)-*N*-ethylphenothiazine (BCF3EPT).

## Experimental

### Materials

Ethylene carbonate (EC), ethyl methylcarbonate (EMC), and  $\text{LiPF}_6$  were purchased from BASF Corporation. The maximum water content in the carbonate solvents is 20 ppm, determined by assay at BASF. DBB was purchased from 3M. EPT and BCF3EPT were synthesized as previously reported.<sup>17,19</sup>

### Electrochemical Analysis

Cyclic voltammetry measurements were performed at rt (18–23 °C) using a CH Instruments 605E potentiostat with a three-electrode cell, 3 mm diameter glassy carbon working electrode (polished over a microcloth polishing pad wetted with distilled water and after adding small amount of 0.05  $\mu\text{m}$  gamma alumina powder), Pt wire counter electrode, and Li reference electrode in 1.2 M  $\text{LiPF}_6$  in EC/EMC (3:7 wt. ratio) containing 0.08 M analyte. Diffusion coefficients were calculated from voltammograms recorded at scan rates of 5 to 500 mV/s. The resulting slope of the cathodic and anodic peak currents versus the square root of the scan rate was then substituted into the Randles-Sevcik equations.<sup>20–22</sup>

### Battery Cycling

Overcharge tests were conducted by assembling 2032 coin cells in an argon-filled glove box using  $\text{LiFePO}_4$  cathodes (Piotrek, data obtained from SEM: average particle size 350 nm, coating thickness 65  $\mu\text{m}$ , loading 12  $\text{mg}/\text{cm}^2$ ) and MAG-10 graphite anodes (Hitachi, data provided by supplier: average particle size 10  $\mu\text{m}$ , coating thickness 38  $\mu\text{m}$ , loading 4.88  $\text{mg}/\text{cm}^2$ ), sandwiched around a microporous PP/PE/PP trilayer separator from Celgard (2325, 25  $\mu\text{m}$  thickness, 39% porosity). The electrodes were punched into 1.4 cm circles. The electrolyte contained 0.08 M redox shuttle in 1.2 M  $\text{LiPF}_6$  in EC/EMC (3:7 wt. ratio). A Maccor 4200 cycler was used to perform battery cycling. In one procedure, coin cells were charged at a constant current of C/10 for 60 h, followed by a 2 min rest and 25 h at C/5 or until 5.0 V was reached. In another procedure, coin cells were charged constantly at C/10 until 5.0 V was reached. All tests were performed at rt.

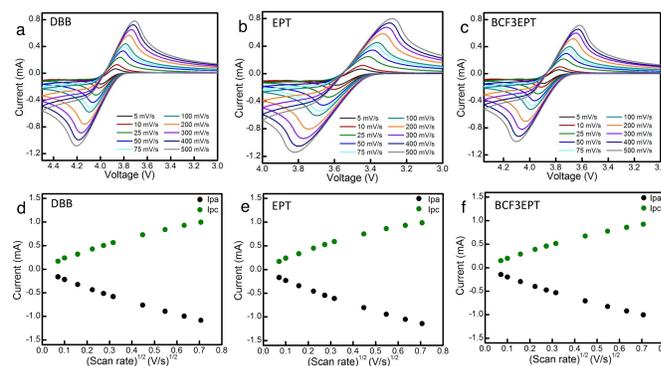
### UV-vis Absorption Spectroscopy

For UV-vis spectra of neutral compounds, redox shuttles were dissolved at 0.2 mM in 1.2 M  $\text{LiPF}_6$  in EC/EMC (3:7 wt. ratio) in an argon-filled glove box in special optical glass cuvettes (Starna) and were removed after sealing with Teflon caps. For UV-vis spectra of radical cations, 70  $\mu\text{L}$  of a 13 mM solution of tris(2,4-dibromophenyl)ammonium hexachloroantimonate in 1.2 M  $\text{LiPF}_6$  in EC/EMC (3:7 wt. ratio) was added to 2.94 mL of a 0.2 mM solution of redox shuttle in the same electrolyte in special optical glass cuvettes. The cuvettes were capped and rotated to distribute the oxidant, and spectra were collected on an Agilent 8453 diode array spectrometer.

## Results and Discussion

Cyclic voltammograms of 0.08 M DBB, EPT, and BCF3EPT were recorded in 1.2 M  $\text{LiPF}_6$  in EC/EMC (3:7 wt. ratio) (Figures 2a–c), a common battery electrolyte. Oxidation potentials vs.  $\text{Li}^{+/0}$  at 0 V were calculated as an average of the anodic and cathodic peak potentials from voltammograms recorded at 100 mV/s (Table 1). Although the oxidation potential of EPT (3.4 V) is too low for

application in  $\text{LiFePO}_4$  batteries, we used EPT as a benchmark because of its structural similarities to BCF3EPT. DBB, however, provides a more practical comparison because of its similar oxidation potential (3.9 V) to that of BCF3EPT (3.8 V), and both compounds have appropriate oxidation potentials for use in  $\text{LiFePO}_4$  batteries. The linear relationship of peak maxima versus square root of scan rate for voltammograms collected from 5 to 500 mV/s (Figures 2d–f) suggests that the experiments were diffusion-controlled. Diffusion coefficients of the neutral compounds ( $0.8\text{--}1.0 \times 10^{-6} \text{ cm}^2/\text{s}$ ) and their oxidized forms ( $0.6\text{--}0.7 \times 10^{-6} \text{ cm}^2/\text{s}$ ) were similar for all redox shuttles (Table 1).



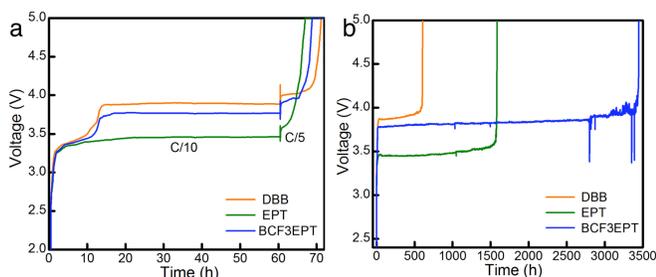
**Fig. 2** Cyclic voltammograms of DBB (a), EPT (b), and BCF3EPT (c) at 0.08 M in 1.2 M  $\text{LiPF}_6$  in EC/EMC at scan rates from 5 to 500 mV/s and plots of forward (black) and reverse (green) peak current vs. square root of scan rate for DBB (d), EPT (e), and BCF3EPT (f).

**Table 1** Half-wave oxidation potentials vs.  $\text{Li}^{+/0}$  at 0 V calculated at 100 mV/s, and diffusion coefficients of the neutral forms and radical cations of DBB, EPT, and BCF3EPT at 0.08 M in 1.2 M  $\text{LiPF}_6$  in EC/EMC. Time spent in overcharge at 0.08 M in  $\text{LiFePO}_4$ /graphite coin cell batteries.

Compound	$E_{1/2}^{+/0}$ vs. $\text{Li}^{+/0}$ (V)	$D_N$ ( $\times 10^{-6} \text{ cm}^2/\text{s}$ )	$D_O$ ( $\times 10^{-6} \text{ cm}^2/\text{s}$ )	Time spent in overcharge (h)
DBB	3.9	0.9	0.7	606
EPT	3.5	1.0	0.7	1580
BCF3EPT	3.8	0.8	0.6	3448

To determine what charging rate to use in long-term constant-charge experiments, the performance of  $\text{LiFePO}_4$ /synthetic graphite coin cells containing 0.08 M DBB, EPT, or BCF3EPT in 1.2 M  $\text{LiPF}_6$  in EC/EMC were tested at variable charging rates. Batteries were programmed to charge at a rate of C/10 for 60 h or until 5.0 V was reached, and then at C/5 for 25 h or until 5.0 V was reached, etc. These batteries have charging capacities of 2 mAh at C/10 and 1.6 mAh at C/5. All cells survived the C/10 charging step, showing overcharge protection at voltages consistent with the oxidation potentials observed in cyclic voltammetry, and all cells reached 5.0 V within 5 to 10 h of cycling at a rate of C/5 (Figure 3a). Since none of the redox shuttles showed extensive protection at this concentration at C/5, we performed subsequent tests at C/10, programming the battery cycler to charge at C/10 until batteries reached 5.0 V. As shown in Figure 3b, the battery containing DBB failed the earliest, at 606 h, followed by the battery containing EPT at 1580 h. The BCF3EPT battery survived the longest at 3448 h, the equivalent of 345 cycles of 200% charge per cycle, or 100% overcharge per cycle (at C/10, 100% overcharge requires 10 h of

charging per cycle;  $3448 \text{ h} \div 10 \text{ h}$  per overcharge cycle = 344.8 cycles, rounded to 350 cycles).



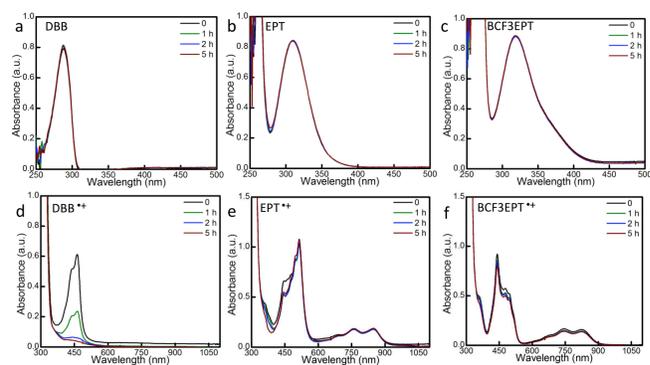
**Fig. 3** Constant charging of coin cells containing 0.08 M DBB, EPT, or BCF3EPT in 1.2 M LiPF<sub>6</sub> in EC/EMC. (a) Plots of voltage vs. time for cells programmed to charge at C/10 for 60 h, then C/5 for 25 h or until 5.0 V was reached. (b) Plots of voltage vs. time for cells programmed to charge at C/10 until 5.0 V was reached (BCF3EPT is still running). Note the difference in ranges of the x-axes.

Although DBB has been reported to survive for as many as ca. 300 cycles at 200% charge per cycle,<sup>9</sup> our results show shorter durations of overcharge protection (equivalent to 60 cycles at 200% charge). However, our results are *not* inconsistent with previously-reported results due to differences in testing conditions. To our knowledge, no one has reported overcharge performance of 0.08–0.1 M DBB in LiFePO<sub>4</sub>/graphite batteries containing >1.0 M of any lithium salt. One report of the overcharge performance of DBB in LiFePO<sub>4</sub>/graphite batteries containing 0.08 M redox shuttle employed a different lithium salt at a lower concentration, specifically 0.7 M lithium bis(oxalate) borate (LiBOB).<sup>9</sup> When our concentration of LiPF<sub>6</sub> is reduced to 0.5 M, the length of constant overcharge protection seen in LiFePO<sub>4</sub>/graphite batteries containing 0.08 M DBB increases to 2058 h, approaching the value reported for DBB with 0.7 M LiBOB.

Our observation of EPT protecting for 1580 h (equivalent of 158 cycles at 200% charge or 100% overcharge) was similar to the maximum number of cycles reported for EPT (150), but this latter value was reported for 0.08 M EPT measured in LiFePO<sub>4</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> batteries containing 0.7 M LiBOB. When EPT was tested using the same electrodes as we chose (LiFePO<sub>4</sub>/graphite), the number of overcharge cycles reported was only 18.<sup>12</sup> EPT survived significantly longer in constant overcharge than we anticipated, and also survived longer than our own previous report of 20 to 65 overcharge cycles using the same electrodes and electrolyte,<sup>17</sup> which emphasizes the importance of fabricating batteries at the same time with the same electrodes and electrolytes for greater consistency in conditions.

The diffusion coefficients of each compound measured at 0.08 M in battery electrolyte show little variation, for which reason we thought that the differences in overcharge performance must be related to the stability of the compounds, either in the neutral or radical cation state. The lower stability of EPT relative to BCF3EPT can be predicted by the presence of CF<sub>3</sub> substituents *para* to the N atom in BCF3EPT; the substituents serve to block these reactive positions from nucleophilic attack in the radical cation state and thereby prevent dimerization. However, the reactivity of DBB relative to BCF3EPT is more difficult to predict because the structures are quite different. We studied the stability of each compound's neutral and radical cation forms in battery electrolyte by UV-vis spectroscopy in case the data could shed light on the relative stability of these redox shuttles.

To compare the relative stability of the neutral compounds, solutions of redox shuttles were prepared at 0.2 mM, a concentration that resulted in absorption values around 0.8. Absorption spectra of the neutral compounds at 0.2 mM are shown in Figures 4a-c. The spectra show little change over 5 h and do not explain the differences in performance of DBB versus BCF3EPT. Next the radical cations of DBB, EPT, and BCF3EPT were generated at 0.2 mM in electrolyte by adding a solution of tris(2,4-dibromophenyl)ammonium hexachloroantimonate in 1.2 M LiPF<sub>6</sub> in EC/EMC to a solution of redox shuttle in the same electrolyte. Spectra recorded immediately after addition of the oxidant and collected through 5 h are shown in Figures 4d-f. While the spectra of EPT and BCF3EPT show only minor changes in the region of radical cation absorption, the absorption intensity of DBB decreases dramatically within 1 h, with almost complete decay occurring within 2 h. This result indicates that the radical cation of DBB is significantly less stable in 1.2 M LiPF<sub>6</sub> in EC/EMC than the radical cations of EPT and BCF3EPT, which could explain why DBB does not protect as long in our batteries at 0.08 M redox shuttle.



**Fig. 4** Absorption spectra of neutral DBB (a), EPT (b), and BCF3EPT (c) at 0.2 mM, and of the radical cations of DBB (d), EPT (e), and BCF3EPT (f) at 0.2 mM in 1.2 M LiPF<sub>6</sub> in EC/EMC.

## Conclusions

BCF3EPT was evaluated as a redox shuttle for LiFePO<sub>4</sub>/graphite batteries in side-by-side experiments with DBB and EPT as benchmarks. The oxidation of BCF3EPT is reversible at high concentrations in battery electrolyte, and the diffusion coefficients of the neutral and oxidized forms are comparable to the relatively robust redox shuttles DBB and EPT. Relative to DBB and EPT, BCF3EPT protects batteries from overcharge for ca. 5 times and 2 times longer, respectively, in constant-overcharge experiments at a charging rate of C/10. UV-vis studies indicate that BCF3EPT and EPT are significantly more stable than DBB in their radical cation states at 0.2 mM in this battery electrolyte. It was not surprising that the stability of their radical cation forms provided more differentiation among the three redox shuttles than did that of their neutral forms, since radical cations are electron-deficient and generally more reactive.

## Acknowledgements

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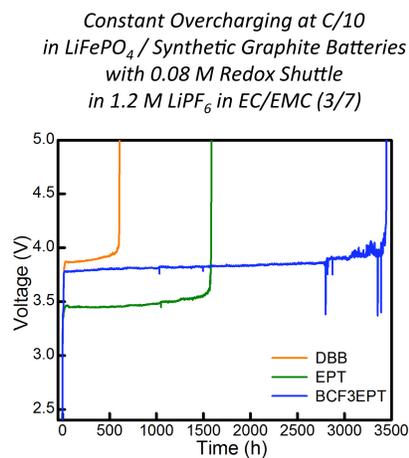
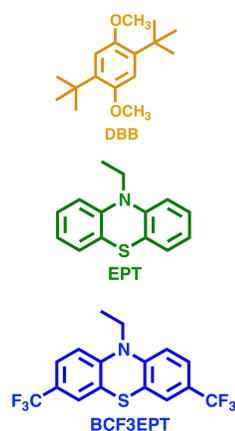
cycler components. We thank Celgard for their donation of battery separators.

## Notes and references

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- 17 S. Ergun, C. F. Elliott, A. P. Kaur, S. R. Parkin and S. A. Odom, *Chem. Commun.*, 2014, **50**, 5339.
- 18 BCF3EPT finished cycling at 242 cycles relative to EPT, which failed at most at 65 cycles in LiFePO<sub>4</sub>/graphite batteries with both redox shuttles at 0.08 M in 1.2 M LiPF<sub>6</sub> in EC/EMC (3:7 wt. ratio) and at charge/discharge rates of C/10.
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## Graphical Abstract



Constant overcharging of  $\text{LiFePO}_4$  / synthetic graphite lithium-ion batteries in which the electrolyte additives 1,4-di-*tert*-butyl-2,5-dimethoxybenzene (DBB), *N*-ethylphenothiazine (EPT), and 3,7-bis(trifluoromethyl)-*N*-ethylphenothiazine (BCF3EPT) limit battery voltage for varying amounts of time.