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Overcharge protection of lithium-ion batteries above 4 V with a perfluorinated phenothiazine derivative†

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Electron-withdrawing substituents are introduced onto the pheno-thiazine core to raise its oxidation potential for use as a redox shuttle in high-voltage lithium-ion batteries. A perfluorinated derivative oxidizes at 4.3 V *vs.* Li$^{+/0}$, and functions for *ca.* 500 h of 100% overcharge in LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$/graphite coin cells at a charging rate of C/10.

The prevention of overcharge, a condition in which a cell's potential rises above the end-of-charge potential of its cathode, is critical to achieving long lifetimes and averting catastrophic failure in lithium-ion batteries (LIBs).[1,2] Batteries connected in series are especially vulnerable to overcharge when mismatches in capacity occur. The condition may be forestalled by introducing additional external circuitry to monitor individual cell potentials in a battery pack, or by integrating internal safeguards to prevent undesirably high potentials from being reached. One such approach involves incorporating additives into the battery electrolyte to mitigate excess applied current by shuttling charge between electrodes.[3,4] These additives, called redox shuttles, oxidize at the cathode/electrolyte interface when the cell potential reaches the oxidation potential of the additive; then, after diffusing to the anode/electrolyte interface, they reduce back to the neutral form. Each cycle sees an electron transported from the anode to the cathode without shorting the cell.

Redox shuttles were first demonstrated as a protective mechanism in LIBs by Dahn and coworkers in 2005; the most successful early shuttles included derivatives of phenothiazine,[5] dialkoxybenzene,[3,6,7] 2,2,6,6-tetramethylpiperinyl oxide (TEMPO),[8] and triphenylamine.[9] In the decade since Dahn's initial reports, redox shuttles have enabled protection against overcharge for time periods equivalent to 300 or more charging cycles and at

charging rates as high as 1C.[7,10,11] Notable examples of redox shuttles that provide extensive overcharge protection at potentials appropriate for the commercially-utilized LiFePO$_4$ (LFP) cathode include 1,4-di-*tert*-butyl-2,5-dimethoxybenzene,[3,6,7] 1,4-di-*tert*-butyl-2,5-bis(2-methoxyethoxy)benzene,[12] and a related imidazolium-functionalized ionic liquid salt.[13,14] More recently, our group reported *N*-ethyl-3,7-bis(trifluoromethyl)phenothiazine (BCF3EPT, Fig. 1) as a highly soluble redox shuttle that provides extensive overcharge protection for the LFP cathode in LIBs, even at high charging rates.[10,11,15]

Despite the extensive overcharge protection capabilities observed for dimethoxybenzene and phenothiazine derivatives in LFP-based batteries, even at concentrations as low as 0.05 to 0.1 M, these compounds oxidize at potentials too low to be used
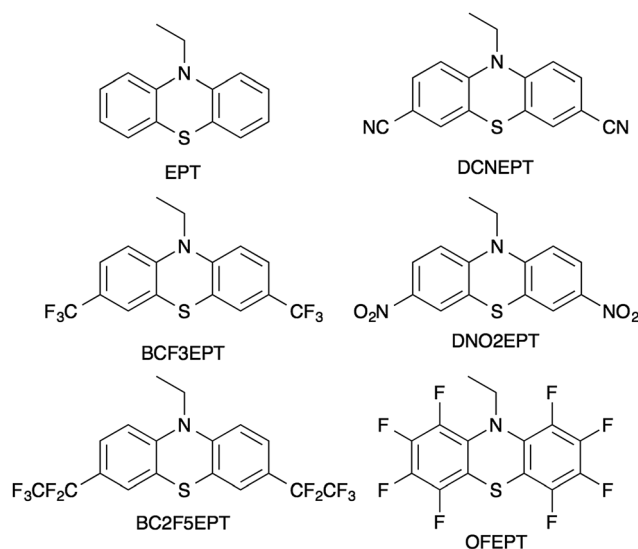
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Fig. 1 Chemical structures of *N*-ethylphenothiazine (EPT) and derivatives *N*-ethyl-3,7-bis(trifluoromethyl)phenothiazine (BCF3EPT), *N*-ethyl-3,7-bis(pentafluoroethyl)phenothiazine (BC2F5EPT), 3,7-dicyano-*N*-ethylphenothiazine (DCNEPT), *N*-ethyl-3,7-dinitrophenothiazine (DNO2EPT), and *N*-ethyl-1,2,3,4,6,7,8,9-octafluorophenothiazine (OFEPT).

with high-voltage cathodes like $LiMn_2O_4$ (LMO), $LiCoO_2$ (LCO), $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). These cathode materials require redox shuttles that oxidize at potentials of at least 4.3 V vs. $Li^{+/0}$, as the end-of-charge potentials for LMO, NMC and NCA lie between 4.1 and 4.2 V.[16] Dahn, Amine, and Zhang have reported redox shuttle candidates with oxidation potentials ranging from 4.0 to 4.8 V vs. $Li^{+/0}$, including 1,4-di-tert-butyl-2,5-bis(2,2,2-trifluoroethoxy)benzene,[17,18] octafluoronaphthalene,[18] 2-methoxyhexafluoronaphthalene,[18] tetraethyl-1,4-di-tert-butyl-2,5-phenylene diphosphate,[19] and 1,4-bis(di-iso-propyl)phosphinyl-2,5-dimethoxybenzene.[20] Although all five compounds protect high-voltage cathodes from overcharge, when paired with graphitic anodes, even the most robust shuttle is limited to a few dozen cycles of protection against 100% overcharge in LFP/graphite cells.

Our recent work with phenothiazine-based redox shuttles led to the development of stable materials with a variety of oxidation potentials.[10,11,15,21,22] The derivatives with the highest oxidation potentials are 3,7-disubstituted derivatives of N-ethylphenothiazine (EPT) containing trifluoromethyl (BCF3EPT) or cyano (DCNEPT) groups, with oxidation potentials of 3.83 and 3.90 V vs. $Li^{+/0}$, respectively (Fig. 1, Table 1).[10,11,15] Attempting to achieve overcharge protection at higher potentials, we synthesized redox shuttles with less electron-rich cores (phenoxazine and carbazole) but found that these compounds failed earlier in overcharge tests than their phenothiazine-based counterparts.[23] Introduction of electron-withdrawing substituents at the N and S positions likewise increases oxidation potentials but yields less stable radical cations with correspondingly limited overcharge protection capability.[24] From these results, we thought it important to retain the electron-rich phenothiazine core and stable N substituents (ethyl, iso-propyl, phenyl), and instead focus on varying the substituents on the aromatic carbon atoms of the phenothiazine ring. This communication summarizes recent attempts to attain stable phenothiazine derivatives for high-voltage overcharge protection by exploring perfluoroalkyl, nitro, or perfluoro substitution of the aromatic periphery. Herein we report the synthesis and characterization of the

following new redox shuttle candidates explored for overcharge protection of high-voltage cathodes: N-ethyl-3,7-bis(pentafluoroethyl)phenothiazine (BC2F5EPT), N-ethyl-3,7-dinitrophenothiazine (DNO2EPT), and N-ethyl-1,2,3,4,6,7,8,9-octafluorophenothiazine (OFEPT) (Fig. 1).

The structures of our new derivatives were inspired by the results of density functional theory (DFT) calculations, which we used to compute adiabatic ionization potentials (IPs). We found a good correlation between calculated adiabatic IPs and oxidation potentials for previously-reported phenothiazine derivatives,[15,21,22] and have since made use of the hybrid B3LYP density functional in conjunction with the 6-311G(d,p) basis set to predict these values prior to synthesis.[25] The results of our calculations for new candidates are summarized in Table 1, along with adiabatic IPs for previously reported EPT, BCF3EPT, and DCNEPT at the same level of theory.

The results of our DFT calculations suggest that BC2F5EPT would oxidize at a potential higher than BCF3EPT ($E_{1/2}^{+/0} = 3.83$ V vs. $Li^{+/0}$) but lower than DCNEPT ($E_{1/2}^{+/0} = 3.90$ V), and that both DNO2EPT and OFEPT would oxidize at potentials higher than DCNEPT. Although we were most curious about DNO2EPT and OFEPT for high-voltage applications, we noted that BC2F5EPT might be practical for protection of LFP-based batteries or for other applications requiring stable electro-active materials. In addition to overcharge protection, highly stable electro-active species such as those listed above are of interest for use in nonaqueous RFBs,[26–29] lithium–air batteries,[30] and photo-redox catalysis.[31,32] We therefore synthesized all three compounds with the expectation that DNO2EPT and OFEPT would be the most promising candidates for high-voltage overcharge protection.

We synthesized DNO2EPT and BC2F5EPT from phenothiazine in two and three steps respectively, as shown in Scheme 1. To prepare DNO2EPT, phenothiazine was doubly nitrated with sodium nitrate in acetic acid following a previously reported procedure;[33] deprotonation of the product and treatment with bromoethane afforded the desired redox shuttle candidate. To synthesize BC2F5EPT, we deprotonated phenothiazine with sodium hydride and added bromoethane to alkylate the N position, yielding EPT; dibromination of the product was performed using N-bromosuccinimide as previously reported.[15] The dibrominated product was then treated with sodium pentafluoropropionate under conditions similar to those employed in our previous synthesis of BCF3EPT to afford BC2F5EPT.[15]

OFEPT was prepared in a convergent, multi-step synthesis in which the phenothiazine core was built from fluorinated benzene derivatives, as shown in Scheme 1. 2,3,4,5-Tetrafluoroaniline was brominated, and the product was combined with bis(2,3,4,5,6-pentafluorothiophenolate) copper(II), the latter of which was prepared from 2,3,4,5,6-pentafluorophenylthiol via treatment with Cu_2O. The resulting copper complex and aryl bromide reacted to form a thioether bridging two fluorinated phenyl rings, one of which contained a primary amine at the position ortho to S. The phenothiazine ring was closed upon deprotonation of the aniline, reacting the amide ion with an sp^2-hybridized C atom ortho to S on an adjacent ring.[34,35] Lastly, an alkylation reaction afforded OFEPT.
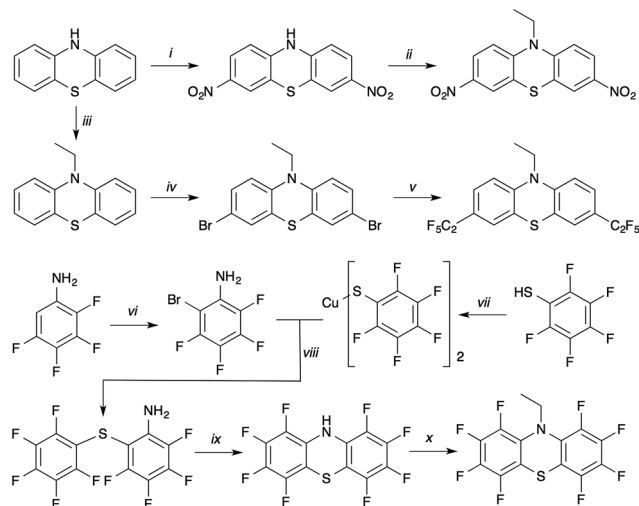
Table 1 Calculated adiabatic IPs, and half-wave oxidation ($E_{1/2}^{+/0}$) and peak values of the potential of the forward wave of first reduction events ($E_{p}^{0/-}$) for EPT, 3,7-disubstituted EPT derivatives, and OFEPT vs. $Li^{+/0}$ at 0 V

Compound	Calculated adiabatic IP (eV)[a]	$E_{1/2}^{+/0}$ vs. $Li^{+/0}$ (V)[b]	$E_{p}^{0/-}$ vs. $Li^{+/0}$ (V)[b]
EPT	6.48	3.51	N/A
BCF3EPT	7.06	3.83	N/A
BC2F5EPT	7.16	3.86	N/A
DCNEPT	7.30	3.90	0.76[c]
DNO2EPT	7.50	3.97	2.39[c]
OFEPT	7.55	4.30	0.52[c]

[a] Adiabatic IPs calculated at the B3LYP/6-311G(d,p) level of theory. [b] Potentials of redox events obtained from cyclic voltammograms recorded in 1.2 M $LiPF_6$ in EC/EMC (3 : 7 wt ratio) at 100 mV s^{-1}. [c] Denotes that the event was irreversible.

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Scheme 1 Synthetic routes to obtain DNO2EPT, BC2F5EPT, and OFEPT. Reagents: (i) $NaNO_2$, AcOH, $CHCl_3$, rt, 1 h, (ii) NaH, DMF, EtBr, 60 °C, 6 h, (iii) NaH, DMF, EtBr, 60 °C, 6 h, (iv) NBS, DMF, o/n, (v) $NaOCOC_2F_5$, CuI, NMP, 180 °C, 2 days, (vi) Fe, NaOAc, AcOH, Br_2, 50 °C, 3 h, (vii) Cu_2O, ethanol, reflux, 5 h, (viii) anhydrous DMF, reflux, 2 h, (ix) NaH, anhydrous dioxane, reflux, 4 h, and (x) NaH, DMF, EtBr, 60 °C, 12 h.

Fig. 2 Cyclic voltammograms of BC2F5EPT, DNO2EPT, and OFEPT at *ca.* 0.3 mM in 1.2 M $LiPF_6$ in EC/EMC (3 : 7 wt ratio) at a scan rate of 100 mV s^{-1} with a glassy carbon working electrode, Pt wire counter electrode, and Li foil reference electrode.

See the ESI† for detailed procedures and structural characterization of all three redox shuttle candidates.

We measured electrochemical potentials and analyzed the reversibility of redox events using cyclic voltammetry (CV) in 1.2 M $LiPF_6$ in ethylene carbonate/ethylmethyl carbonate (EC/EMC, 3 : 7 wt ratio). CV experiments of redox shuttle candidates BC2F5EPT, DNO2EPT, and OFEPT revealed reversible first oxidation events at 3.86, 3.97, and 4.30 V, respectively, *vs.* Li$^{+/0}$ (Fig. 2). The correlation between calculated adiabatic IPs and first oxidation potentials is generally good for EPT and the 3,7-disubstituted derivatives shown in Fig. 1, affording an R^2 value of 0.947 for the line of best fit (Fig. S4†). The oxidation potential of OFEPT is higher than expected from the trend exhibited by the 3,7-disubstituted derivatives, and a lower R^2 value (0.906) results when OFEPT is included (Fig. S5†).

We also performed CV experiments over a wider electrochemical window (0.4–5.0 V, Fig. S2†). First we scanned for an electrochemical window of 3.0–5.0 V (higher), looking for oxidation events, and then from 3.0–0.4 V (lower) looking for reduction events. Scanning to higher potentials revealed that all compounds display an irreversible second oxidation at or above 4.5 V. Scanning to lower potentials leads to cathodic currents produced from reduction of DNO2EPT and OFEPT. For DNO2EPT, irreversible reduction events were observed at 2.39 and 2.06 V. For OFEPT, an irreversible reduction was observed at 0.52 V. The high reduction potential of DNO2EPT suggests that its use in LIBs containing graphitic electrodes would be impractical because reduction of the neutral compound to the radical anion would occur during charging, leading to decomposition of the redox shuttle and/or limiting charging potential. Reduction of OFEPT during charging is also a possibility, but precedence suggests that it may not be detrimental to
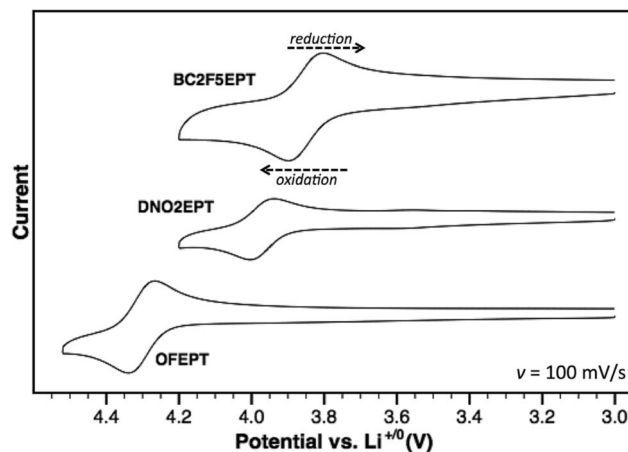
performance: in a prior study, we found a redox shuttle with a low-potential reduction event that nonetheless exhibited a faculty for overcharge protection in LIB coin cells containing graphitic electrodes.[21]

We now turn to overcharge tests in coin cell batteries in which redox shuttles were cycled at 100% overcharge. Under this procedure, 200% of the current needed to reach the end-of-charge potential of the cathode is applied, following which the cell is discharged. This cycle of charge–overcharge–discharge is repeated until the redox shuttle can no longer mitigate current and the cell potential rises to 5 V. In these experiments, only a few hours of the first 200% charge cycle are spent in overcharge due to the longer time required to reach the shuttle potential as a result of SEI formation. Starting in the second cycle, the cells spend *ca.* 10 h in charge, 10 h in overcharge, and 10 h in discharge.

OFEPT was our only viable redox shuttle candidate for use with high-voltage cathodes; both BC2F5EPT and DNO2EPT are too easily oxidized. For the latter compounds, we attempted to perform overcharge tests instead with LFP/graphite cells, although DNO2EPT's performance could not be studied due to its limited solubility. By contrast, BC2F5EPT is highly soluble, dissolving at 1 M (30 wt%) in carbonate-based electrolytes. In these initial cycling tests, BC2F5EPT's performance was unremarkable for an LFP shuttle, surviving a mere 17 cycles of 100% overcharge cycling before reaching 5 V (Fig. S6†). Perhaps a different shuttle concentration or electrolyte environment could lead to more extensive cycling.

Ultimately our interest lies in achieving overcharge protection when high-voltage cathodes such as LMO, LCO, NMC, and NCA are used in LIBs. To test overcharge performance, we used NCA/graphite coin cells. OFEPT's oxidation potential of 4.30 V is ideal for NCA cathodes, and the compound readily dissolves at 0.5 M (13 wt%) in carbonate-based electrolytes. Here we cycled NCA/graphite coin cells containing OFEPT at 0.08 M for consistency with previous redox shuttle studies. The overcharge

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cycling results for OFEPT in an NCA/graphite coin cell are shown in Fig. 3. Here we observed OFEPT to protect cells from overcharge at potentials ranging from 4.2–4.3 V, demonstrating the first example of a phenothiazine derivative that protects a high-voltage cathode from overcharge.

During cycling, the discharge capacity decreased by 7%; the decrease in charge capacity is equalized by increased overcharge protection, perhaps due to the effect of the abusive cycling conditions on electrode stability. Hence the cell capacity faded slowly upon extended cycling in the case of OFEPT. During the 14th overcharge cycle, the potential of the cell during overcharge began to increase. This effect became more pronounced in each subsequent cycle, although the cell potential does not reach 5 V until cycle 17. Although the lifetime for protection is short compared to BCF3EPT and other shuttles used with LFP-containing cells, this performance is in line with recently reported dimethoxybenzene-based redox shuttles used in $LiMn_2O_4/Li$ and $LiMn_2O_4/MCMB$ coin cells.[19,20]

In summary, we synthesized three new phenothiazine derivatives with electron-withdrawing substituents. Of these compounds, the perfluorinated shuttle candidate OFEPT exhibited a reversible oxidation at 4.3 V *vs.* $Li^{+/0}$, making it the first phenothiazine derivative appropriate for overcharge protection for higher-voltage cathodes such as NCA cathodes. Furthermore, this study is only the second to report overcharge protection of NCA-containing cells through the use of redox shuttle additives.[36] Our future studies will probe the decomposition mechanisms of OFEPT to determine whether the shuttle's

structure and/or electrolyte environment – including shuttle concentration – can be modified to further extend overcharge protection of high-voltage cathodes.

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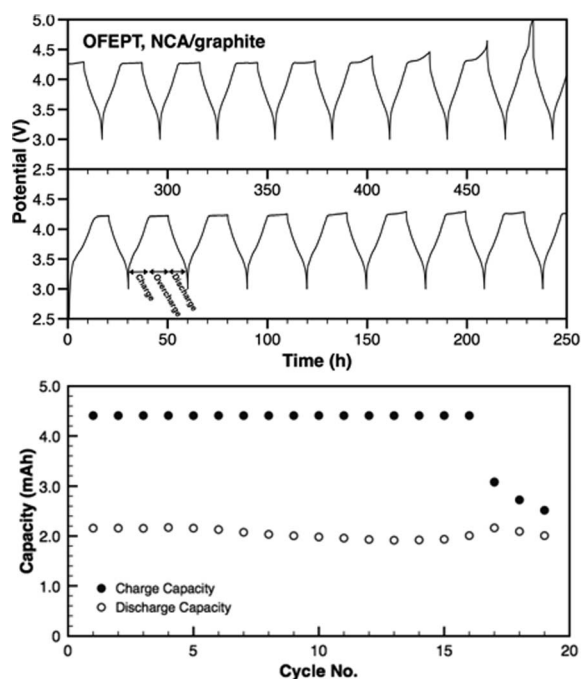
Fig. 3 Top: Potential *vs.* time for 100% overcharge cycling of OFEPT in NCA/graphite coin cells. OFEPT was incorporated into 1.2 M $LiPF_6$ in EC/EMC (3 : 7 wt ratio) at 0.08 M; 100% overcharge cycling was performed at a rate of C/10. Bottom: Charge and discharge capacities *vs.* cycle number for the same cell.

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