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ARTICLE

Overcharge Protection of Lithium-Ion Batteries with Phenothiazine Redox Shuttles

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Overcharge in lithium-ion batteries (LIBs) can be mitigated using electron-donating small molecules with oxidation potentials just above the end-of-charge potential of the electrochemical cell. These additives function by oxidizing at the cathode/electrolyte interface, forming radical cations, and are then reduced at the anode/electrolyte interface, becoming neutral again. A variety of redox shuttles have been reported since 2005 including derivatives of TEMPO, alkoxybenzene, and phenothiazine. This perspective focuses on the phenothiazines redox shuttles and their performance in LIBs.

Introduction

In batteries, the end-of-charge potential is defined as the voltage designated at which an electrochemical cell is fully charged; above this potential, overcharge occurs.¹⁻² In overcharge, undesirable events such as the irreversible over-extraction of lithium from the cathode, and electrolyte oxidation (at the cathode) or reduction (at the anode) occur. These reactions can produce gases, increasing battery pressure, and reactions can be exothermic, raising battery temperature. In the most benign case, battery lifetimes will be compromised; in the most severe cases, cells enter thermal runaway, leading to fires and/or explosions.

Overcharge is specifically a problem when batteries are connected in a series and the voltage of this series is monitored as a group, or pack. Three 4-volt cells in series make a 12-volt battery, for example. If one takes that 12-volt series and charges it to 12 volts, three perfectly normally working batteries would charge to 4 V each. If one of these batteries was damaged during manufacturing or otherwise and its storage capacity was lower than the others, it would reach 4 V before the remaining cells in the series. For that pack to get to 12 V, the potential of the lower capacity, or weaker, battery would exceed 4 V, putting that battery in overcharge. See an illustration of this concept in Figure 1 (top).

A few approaches are used to mitigate overcharge. In one, a battery pack is not charged to its total capacity but rather to some lower percent. This is useful in preventing overcharge in series containing mismatched cells but is also useful in extending pack lifetimes because it prevents cells from reaching the upper potentials that lead to an acceleration of reactions that degrade battery performance. Thus, often a battery pack's capacity is underutilized

in exchange for performance over a longer number of charge/discharge cycles. Another, more expensive approach is to install circuitry that monitors the potential of each individual cell. This route ensures that no individual cell is charged too much: Once one cell reaches its end-of-charge potential, no more current is applied to that series.

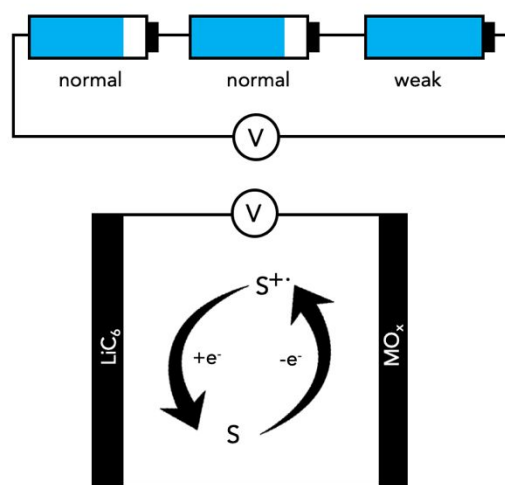


Figure 1. Illustration of (top) overcharge in a battery containing cells in series and (bottom) a redox shuttle functioning in overcharge mitigation.

A final approach to mitigating overcharge is the use of internal shunts called redox shuttles. These shuttles are usually organic compounds that are incorporated into the battery electrolyte at a small weight percent, around 0.1 M, as it is important that the presence of the additive does not decrease the ionic conductivity of the electrolyte. These shuttles lie dormant until the potential of the cathode reaches a value that matches the oxidation potential of the shuttle. Once those potentials match, the redox shuttle is oxidized at the cathode/electrolyte interface, donating an electron to the cathode and – assuming it is an electron-paired neutral species – it

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forms a radical cation. This radical cation migrates to the anode/electrolyte interface and accepts an electron, returning to its neutral state. For every cycle of this electron transfer process depicted in Figure 1 (bottom), one equivalent of electron in current is mitigated. An effective shuttle will stabilize the cell potential at its oxidation potential.

Jeff Dahn of Dalhousie University reported the capabilities of redox shuttles in lithium-ion batteries (LIBs) in 2005.³ Dahn's research spanned the gamut of organic redox-active compounds. In an early publication, they reported the screening of 58 alkoxybenzene compounds.⁴ Around the same time a PhD student was writing a thesis with over a hundred species evaluated.⁵ What resulted from these studies were three successful redox couples: 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), di-*tert*-butyl-2,5-dimethoxybenzene (DDB), and *N*-methylphenothiazine (MPT) (Figure 2).⁶ These redox couples all showed >100 cycles of 100% overcharge protection when incorporated into the electrolyte of Li₄Ti_{5/3}O₂/LiFePO₄ coin cells, and DDB survived >200 cycles with those electrodes and in graphite/LiFePO₄ coin cells.

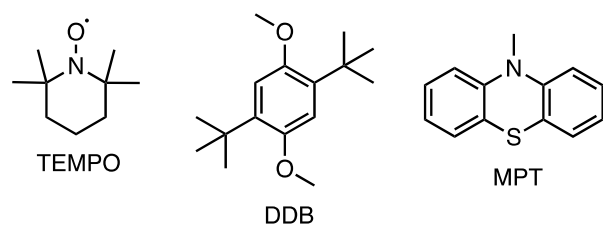


Figure 2. Three of the most effective first redox shuttles: 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), 1,4-di-*tert*-butyl-2,5-dimethoxybenzene (DDB), and *N*-methylphenothiazine (MPT).⁶

Since that work, TEMPO has been functionalized to include derivatives with a carbonyl (oxo), methoxy, cyano, and ester substituents with increased redox potentials,⁷ which is necessary for LiFePO₄-containing cathodes as the redox potential of TEMPO itself lies before the end-of-charge potential of this cathode, meaning that its activation would interfere with the charging process. Similarly DDB derivatives have included functionalization to raise solubility or redox potential with the methyl group replaced with trifluoroethoxy groups,⁸ and phosphonates,⁹ for use with higher potential cathode materials. Further functionalization has included glycol groups¹⁰⁻¹¹ or substituents with permanent charges¹² instead of methoxy groups, in these cases to increase solubility. It wasn't until 2013 that the first publication on new phenothiazine derivatives was published.

This Perspective will provide an overview of phenothiazine redox shuttles, first focusing on derivatives with substituents *para* to the nitrogen atom. Next will be derivatives with variation in alkyl group at the *N* position, which will be followed by perfluorination of the aromatic rings. Lastly to be discussed is the incorporation of sterically bulky groups to increase oxidation potentials via the

prevention of electronic relaxation. In these latter cases, higher potential cathode materials are more appropriate.

Discussion

Para-Substituted Derivatives

In 2013, my group published the first work on phenothiazine redox shuttles since Dahn's initial publications. In this case, we took the core *N*-ethylphenothiazine (EPT) and incorporated a variety of substituents *para* to the nitrogen atom – the 3 and 7 positions. This publication included substituents R = CH₃, Cl, Br, and CF₃ (Figure 3).¹³ In a subsequent publication, we reported EPT with R = OCH₃, which had a lower redox potential than the lowest oxidation potential compound with R = CH₃.¹⁴ The oxidation potentials of these compounds correlate with the adiabatic ionization potentials calculated at the B3LYP-6-31g(d,p) level of theory.

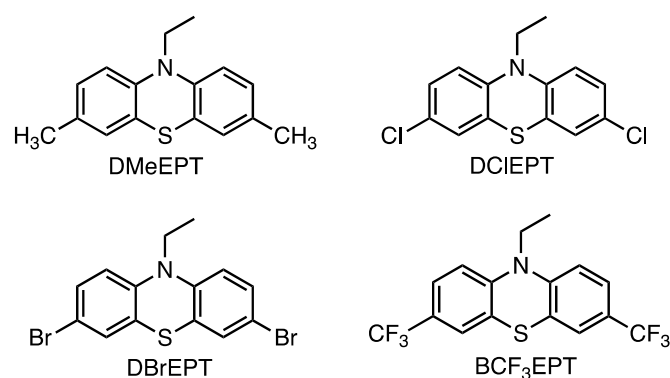


Figure 3. *Para*-substituted *N*-ethylphenothiazine derivatives.

The methyl-substituted derivative DMETPT had an oxidation potential too low to be practical for overcharge protection. We found that the chlorinated and brominated derivatives DCIEPT and DBREPT functioned in overcharge in 1.2 M LiPF₆ in ethylene carbonate / ethyl methylcarbonate (3:7 wt ratio), a common LIB electrolyte, but for a limited number of cycles. We later found, upon examining the full window of the electrolyte, that each compound showed reduction event around 0.3-0.5 V vs. Li^{+/0}, which suggests reduction of the shuttle will occur upon charging the battery.¹⁵ Evidence of molecular decomposition in post-cycled batteries shows dehalogenation of these compounds. Of the *para*-substituted compounds, the redox potential of BCF₃EPT, at 3.83 V vs. Li^{0/+}, was the most appropriate for overcharge protection of LiFePO₄-containing LIBs.¹³ In the 2013 publication, we reported 59 cycles of overcharge protection in an ongoing experiment. Continued cycling of this coin cell resulted in over 380 cycles of 100% overcharge protection prior to shuttle failure.¹⁶ In fact, the cell spent more time in overcharge than in a typical 100% overcharge (or 200% charge) experiment due to the cell losing capacity before the shuttle failed. BCF₃EPT is a highly soluble

compound, which enabled us to assemble coin cells with concentrations of redox shuttle as high as 1.5 M. These high concentrations enabled overcharge protection at high charging currents. At 1 M in concentration, in constant charge experiments, BCF₃EPT was able to mitigate overcharge to currents as high as 1C (Figure 4).

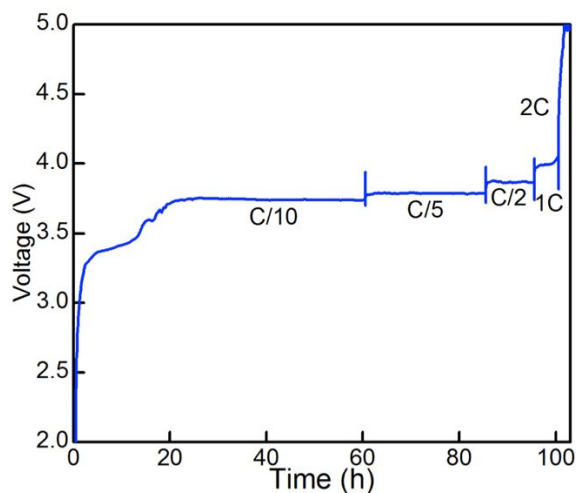


Figure 4. Rate performance for LFP (MTI) / MCMB coin cell containing 1.2 M LiPF₆ in EC/EMC (3:7) and 1.0 M BCF₃EPT.¹⁶

N-Substituted Derivatives

In 2015, our group reported a study of *N*-substituted phenothiazines, which included variably substituted alkyl chains and a phenyl group (Figure 5).¹⁷ We found that redox potentials in LiPF₆/EC/EMC varied based on Hammett constants except in one instance: For tBuPT, the oxidation event occurred at the same potential as PT.

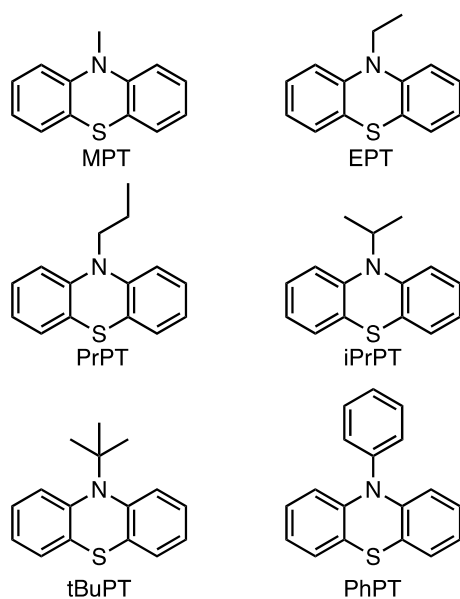


Figure 5. *N*-Substituted phenothiazines.¹⁷

As it turns out, because the *tert*-butyl group can undergo C-N bond cleavage to release a stable, 3° carbocation, in the battery electrolyte, which contains trace HF, the *tert*-butyl group cleaves, leaving behind PT. This does not happen in cyclic voltammetry experiments in dichloromethane (DCM) where trace acid is not an issue. However, analysis of the in situ generated radical cation of tBuPT is unstable in DCM and converts to the PT radical cation, as evidenced by UV-vis spectroscopy (Figure 6). Importantly, this result shows us that *tert*-butyl and other 3° alkyl groups are problematic – at least when connected to nitrogen atoms.

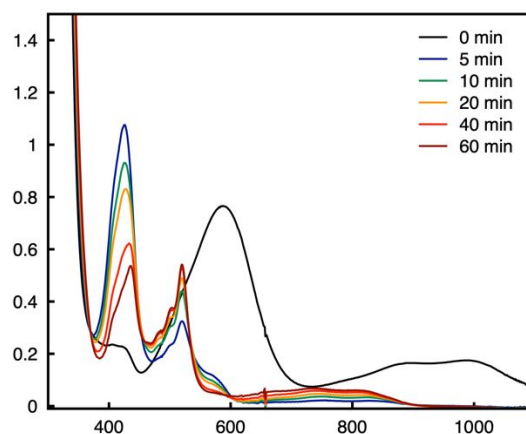


Figure 6. UV-vis absorption spectra showing the conversion of the tBuPT radical cation to the PT radical cation.¹⁷

Next we aimed to increase the redox potential of phenothiazine groups by installing more electron-withdrawing groups onto the periphery of the phenothiazine ring, either with perfluoroethyl or nitro groups *para* to the nitrogen or by perfluorination of the aromatic rings (Figure 7).¹⁸ The perfluoroethyl group only shifted the oxidation potential 0.03 V more positive than the trifluoromethylated version. The dicyanocompound (DCNEPT) with oxidation potential 3.90 V, was too insoluble for use as a shuttle. While the nitrated compound had a higher oxidation potential at 3.97 V vs. Li⁰⁺, irreversible reduction events were observed at 2.06 and 2.39 V. Reduction at the graphitic anode would yield an unstable radical anion, resulting in decomposition of the redox shuttle; further, the high potential reduction event would also prevent a LIB from fully charging. Only the perfluorinated derivative exhibited a reversible redox event above 4 V, at 4.30 V, and had no reduction events in the electrochemical window.

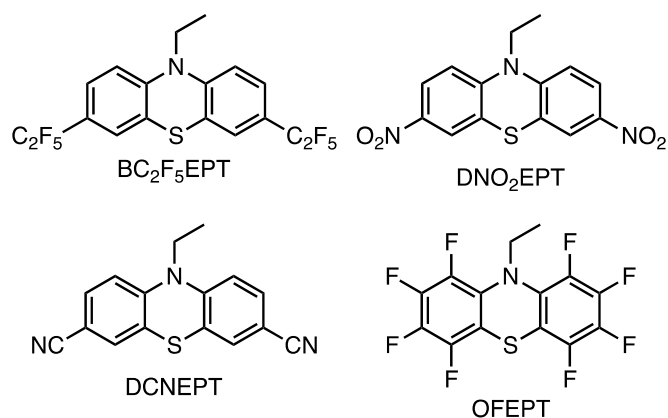


Figure 7. Higher voltage phenothiazines.¹⁸

The performance of the perfluorinated derivative, OFEPT, yielded over 450 h of cycling in 100% overcharge conditions before redox shuttle failure (Figure 8). An observation worth noting is that following redox shuttle decomposition, the LIB is still functional, even when charged to 5 V. This result suggests that OFEPT undergoes a reaction at the cathode/electrolyte interface that passivates this high voltage lithium nickel cobalt aluminum (NCA) cathode. Further evaluation of OFEPT as a high voltage passivating agent is underway.

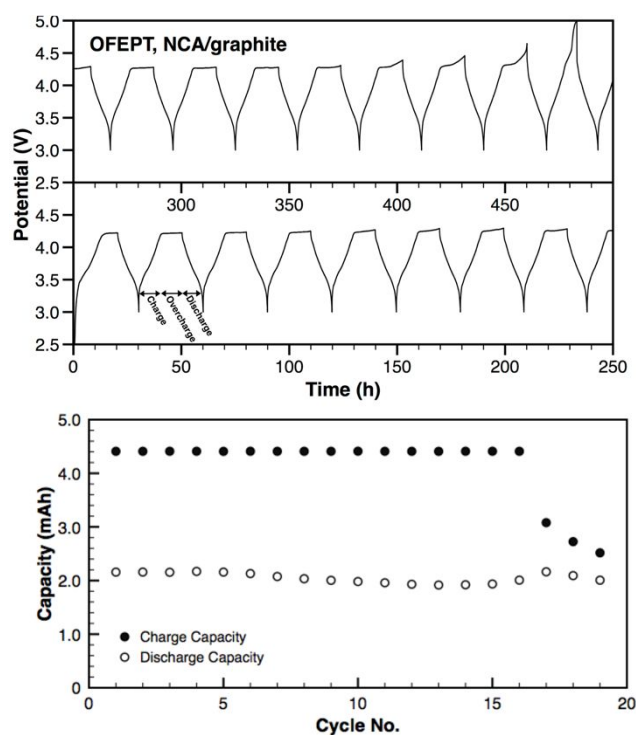


Figure 8. Overcharge protection and subsequent cycling of a NCA/graphite coin cell battery containing 0.08 M.¹⁸

When phenothiazines are oxidized, they undergo a geometric change from having a bent conformation, in which there is about a 135° to 150° bond angle between the two aryl rings, to one in which the aryl rings are or are nearly in the same plane. We showed in 2017 that preventing the geometric

relaxation of the phenothiazine, upon oxidation to its radical cation state, raised the oxidation potential regardless of the Hammett constant of the sterically bulky group preventing relaxation.¹⁹ Consider as an example 3,7-DMeEPT versus its constitutional isomer 1,9-DMeEPT (Figure 9). The 3,7-disubstituted isomer has electron-donating methyl groups at the positions *para* to the nitrogen atom, imparting no strain in the system versus its parent EPT. The oxidation potential becomes 0.14 V less positive for 3,7-DMeEPT, consistent with what one would predict using Hammett constants. However, if one places the same methyl groups in at the 1 and 9 positions, strain is induced and the oxidation potential shifts 0.28 V more positive than parent EPT. This shift in redox potential brings 1,9-DMeEPT within only 0.06 V of BCF₃EPT. The larger the *N* substituent, going from ethyl to *iso*-propyl to phenyl, the more positive the redox potential is, although it is worth noting that cyclic voltammetry of the phenyl-containing compound exhibits an irreversible oxidation.

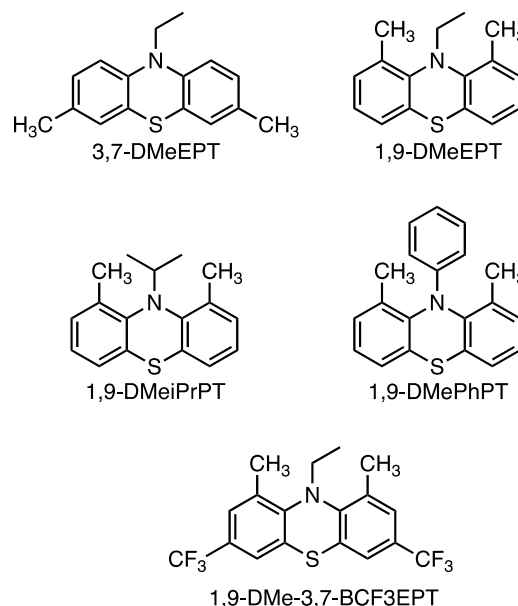


Figure 9. A 3,7-disubstituted EPT derivative, its strained 1,9-disubstituted constitutional isomer, and derivatives thereof.¹⁹⁻²⁰

In 2020, we showed that the effect of sterically bulky substituents and electron-withdrawing groups is additive. With 1,9-DMe-3,7-BCF₃EPT (Figure 9), both types of groups are present, raising the oxidation potential by 0.61 V versus parent EPT, and by 0.17 V versus BCF₃EPT.²⁰ The crystal structure (Figure 10) shows how the strained radical cation relaxes to a geometry of only 162.8°. It is worth noting that this butterfly angle is relaxed compared to the 140.5° angle in the neutral compound.

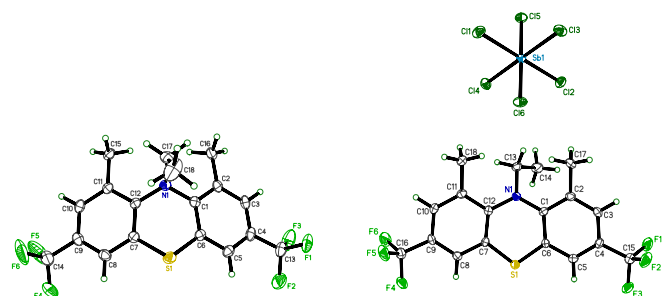


Figure 10. Neutral compound (left) and hexachloroantimonate radical cation salt (right) of 1,9-DMe-3,7-BCF₃EPT.²⁰

While BCF₃EPT shows extensive overcharge protection of LiFePO₄ cathodes, protection of NCA cathodes is limited and new derivatives are needed to meet the lifetime requirements of LIBs. Further, the synthesis of compounds OFEPT and 1,9-DMe-3,7-BCF₃EPT requires numerous steps that are difficult to scale. An improvement in phenothiazine derivatives could be in the design of new compounds with more simple syntheses.

A summary of the oxidation potentials of the phenothiazine derivatives presented here is shown in Table 1. It should be noted that in some cases (the compounds presented in Figure 9), and estimate vs. Li^{+/0} is calculated by adding 3.2 V to the oxidation potential recorded in XXX and referenced to ferrocene/ferrocenium at 0 V.

Table 1. Half-wave oxidation potentials of the compounds reported here vs. Li^{0/+}.

Compound	E _{1/2} ^{0/+}	Compound	E _{1/2} ^{0/+}
MPT	3.55	BCF ₃ EPT	3.83
EPT	3.51	DNO ₂ EPT	3.97
iPrPT	3.59	DCNEPT	3.90
tBuPT	3.45	OFEPT	4.30
PhPT	3.52	1,9-DMeEPT	4.08 ^a
DMeEPT	3.40	1,9-DMeiPrPT	4.06 ^a
DCIEPT	3.64	1,9-DME-3,7-BCF ₃ EPT	4.10 ^a
DBrEPT	3.66		

^aCV was recorded in 0.1 M nBu₄NPF₆ versus Cp₂Fe^{0/+}. Conversion to Li^{0/+} was applied by adding 3.2 V to estimate half wave potentials.

Conclusions

In summary, this perspective shows different ways of modulating the redox potential and stability of phenothiazine-based redox shuttles. These compounds are not only of interest for overcharge protection but have found use as candidates as redox flow battery polysolutes and as shelf-stable chemical oxidants. While the requirements for these applications are different in that polysolutes must also be highly soluble, and for chemical oxidants, stability in the solid state is crucial, all of these uses of electron-donating phenothiazines require stability in the neutral and radical cation forms in solution environments.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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