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Redox Shuttle Additives for Lithium-Ion Battery

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1. Introduction

Overcharge of lithium-ion batteries can be dangerous. Overcharge generally occurs when a current is forced through a cell, and the charge delivered exceeds its charge-storing capability.¹⁻³ Overcharge of lithium-ion batteries can lead to the chemical and electrochemical reaction of batteries components, rapid temperature elevation, self-accelerating reactions, and even explosion.

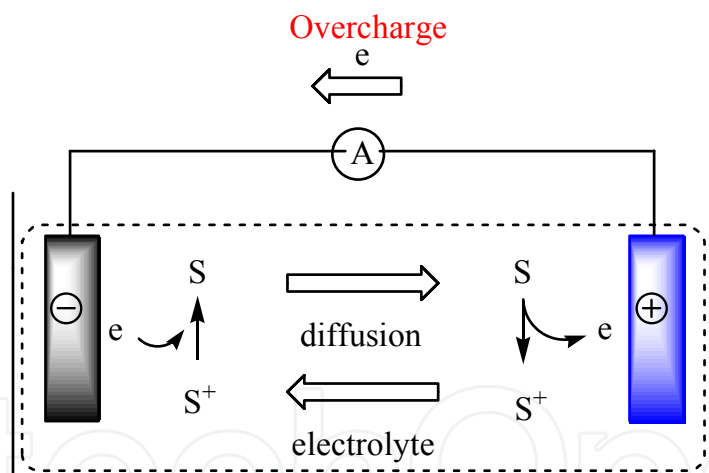


Fig. 1. Mechanism of redox shuttle overcharge protection

Redox shuttle additives have been proposed for overcharge protection of secondary lithium-ion batteries for decades.⁴⁻⁸ Generally, the redox shuttle molecule can be reversibly oxidized and reduced at a defined potential slightly higher than the end-of-charge potential of the cathode. This mechanism can protect the cell from overcharge by locking the potential of the cathode at the oxidation potential of the shuttle molecules. The detailed mechanism is shown in Figure 1. On the overcharged cathode surface, the redox shuttle molecule (S) is oxidized to its (radical) cation form (S^+), which, via diffusion across the cell electrolyte, would be reduced back to its original or reduced state on the surface of the anode. The reduced form would then diffuse back to the cathode and oxidize again. The “oxidation-diffusion-reduction-diffusion” cycle can be repeated continuously due to the reversible

nature of the redox shuttle to shunt the overcharge current. The redox shuttling mechanism at overcharge can be regarded as a controlled internal short, and the net result of the shuttling is to convert the overcharge electricity power into heat, which avoids the reactions that occur between the electrodes and electrolyte at high voltage. Redox shuttles can also be used for automatic capacity balancing during battery manufacturing and repair.

2. Brief history

The research on redox shuttles for overcharge protection of lithium-ion batteries can be traced back to the 1980s, when Behl et al. reported that I⁻/I₂ (**1** in Figure 2) has its first oxidation potential at about 3.25 V vs. Li⁺/Li and, hence, is suitable for overcharge protection of 3-V class lithium batteries.^{9,10} Behl et al. did not fully evaluate the overcharge protection performance due to the lack of a proper cell system and high-voltage limit test procedures; nonetheless, I⁻/I₂ represents the first example that showed promising overcharge protection by using an electrochemical quasi-reversible system in lithium cells. Soon thereafter, Behl evaluated Br⁻/Br₂ (**2** in Figure 2) as a redox shuttle additive and obtained similar results, except for the higher oxidation potential deriving from the more compact electron configuration of the Br atom.¹¹

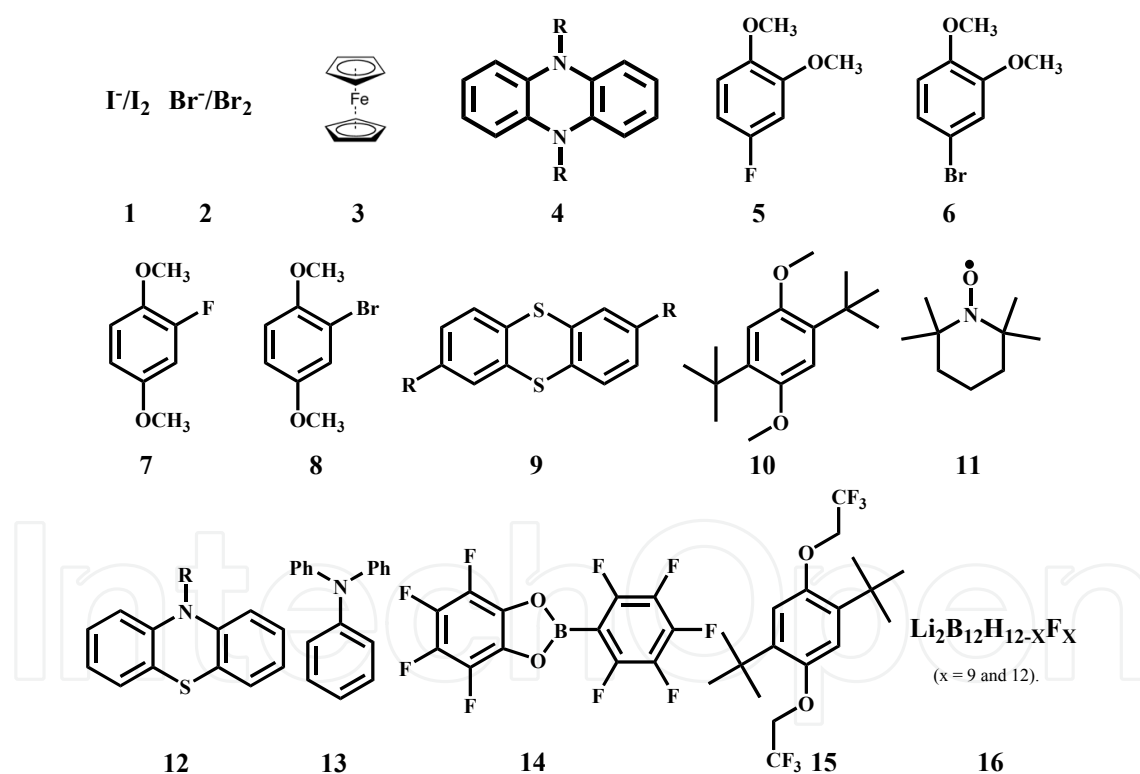


Fig. 2. Representative examples of redox shuttle additives

Later, organometallic ferrocene derivatives were extensively studied as redox shuttles^{6,12} (**3** in Figure 2). Ferrocene can undergo reversible one-electron oxidation to form a stable cation, called “ferrocenium,” and, therefore, is electrochemically reversible.¹³ Some ferrocene derivatives, such as methoxymethylferrocene, carbomethoxyferrocene, carbamoylferrocene, dimethylaminomethylferrocene, and 1,1'-dimethylferrocene,^{6,12} have been investigated to explore their overcharge protection performance. Most of them could provide long

overcharge protection to lithium cells, and by tuning the substituents, upper voltage limits from 3.0 to 3.5 V vs. Li/Li⁺ can be achieved.

Owing to the success with ferrocenes, due to the versatile design and feasible modification, organic systems have drawn more and more attention to the development of novel redox shuttles. In 1999, Delabouglise and co-workers first examined the dihydrophenazine system (**4** in Figure 2) as a redox shuttle.¹⁴ The introduction of alkyl groups into the N atoms played a key role in enhancing the overcharge performance of the dihydrophenazine system.¹⁴ Around the same time, Adachi and co-workers conducted a screening study, investigating a series of metallocene and dimethoxybenzene (**5-8** in Figure 2) derivatives.¹⁵ Metallocene compounds were observed to be electrochemically reversible systems with potentials around 4 V, but the low solubility and large molecular size hindered their overcharge performance in electrolytes. Dimethoxybenzene derivatives, on the other hand, did show promising results, especially for those compounds with methoxy groups at the *ortho* and *para* positions. The substitution of halogen atoms could lift the redox potential to around 4 V. This was the first time that the dimethoxybenzene system was investigated as a redox shuttle candidate.

In 2002, Lee and co-workers discovered a series of thiantlurene derivatives (**9** in Figure 2) that showed potential as redox shuttles for lithium-ion batteries.¹⁶ By introducing acetyl, alkyl, and halogen groups, they developed novel compounds that provide reversible redox potential higher than 4 V, making them applicable to overcharge protection for 4-V cathode materials.

In 2005, Dahn and co-workers screened numerous molecules with various substituents on the aromatic rings.^{17,18} Among them 2,5-di-*tert*-butyl-1,4-dimethoxybenzene (later termed DDB) (**10** in Figure 2) stood out as having excellent overcharge protection performance. DDB is electrochemically reversible at 3.9 V vs. Li/Li⁺ and can provide over 300 cycles of 100% overcharge per cycle for lithium-ion cells with LiFePO₄ as the cathode. The DDB was evaluated to confirm its superior performance in terms of high-rate overcharge protection¹⁹ and overdischarge protection,¹⁷ and a theoretical and mechanistic analysis for its high stability was also conducted.^{18,20,21} Dahn's group later discovered another two stable redox shuttle systems, which are phenothiazine derivatives (**12** in Figure 2) and 2,2,6,6-tetramethylpiperinyl-oxide (TEMPO) (**11** in Figure 2) derivatives. Both systems work well in terms of long-time overcharge protection; for instance, use of 10-methylphenothiazine (MPT) in a cell system provided 153 cycles of 100% overcharge at the C/10 rate, and TEMPO survived 124 cycles. However, the relatively low potentials of these two systems (3.5~3.7 V vs. Li/Li⁺) limit their applications in real batteries. Triphenylamine derivatives (**13** in Figure 2) were later investigated as potential redox shuttle candidates.²² Even though those compounds exhibited reversible cyclic voltammetry signals and tunable redox potentials using various electronic substituents, they are not comparable to DDB in terms of either stability or redox potentials. Because of the lack of a high-potential electrochemically reversible system, the redox potential became a major limitation of the redox shuttles for lithium-ion battery technology. This obstacle remained unresolved until 2007, when Chen and co-workers developed a novel redox shuttle, 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole (PFPTFBB) (**14** in Figure 2), which has a high redox potential of 4.43 V vs. Li/Li⁺.²³ Under various charging rates and aggressive conditions in cell testing with a LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode, PFPTFBB was able to survive after more than 160 cycles with 100% overcharge. PFPTFBB was the first stable redox shuttle that could be used for 4-V class cathodes. In addition, the incorporated boron center of this additive is a strong Lewis acid and can act as an anion receptor to dissolve LiF generated during the operation of lithium-ion batteries, making it a bifunctional electrolyte additive.

Another recent example is 1,4-di-*tert*-butyl-2,5-bis(2,2,2-trifluoroethoxy)benzene (**15** in Figure 2), developed by Dahn's group in 2009.²⁴ This shuttle is a high potential version of DDB and keeps the same redox center structure. The fluoride groups increase the potential to 4.2 V vs. Li/Li⁺, high enough for the LiCoO₂ cathode. However, in half-cell tests with LiCoO₂, this molecule was only able to provide 46 cycles of 100% overcharge at C/10, and no graphite anode full-cell study was reported.

In 2010, Chen and Amine reported another high-potential redox shuttle system, lithium borate cluster salt, Li₂B₁₂H_{12-x}F_x ($x = 9$ and 12) (**16** in Figure 2).²⁵ The redox potential of this molecule can be tuned by the degree of fluorination; therefore, it is possible to design the redox shuttle for various cathode materials. In addition, the form of this lithium salt makes it a bi-functional solute of the electrolyte for long-life and safe lithium-ion batteries.

3. Characteristics of ideal redox shuttles

From this brief history of the development of redox shuttles, some general ideas on what makes an ideal redox shuttle have emerged.

First, redox shuttle molecules have to be electrochemically reversible, which is the most important requirement. From the redox shuttle mechanism shown in Figure 1, the oxidized form of the redox shuttle, i.e., the radical cation for the neutral compound or cation for the TEMPO-type compound has to be stable enough to survive the diffusion circle, which is also a determining factor of an electrochemically reversible system.

Second, the redox potential of the system must be slightly higher than the end of charge potential of the cathode materials, which determines whether or not the redox shuttle could be used for certain cathode materials. According to a previous study,^{7,26} the redox potential of the shuttle additive should be about 0.3–0.4 V above the normal maximum operating potential of the cathode so that the cell can be normally charged before the shuttle molecule begins to function, thereby minimizing the self-discharge effect. Also, the potential should not exceed the electrochemical window of state-of-art electrolytes, i.e., 4.5 V vs. Li/Li⁺;²⁷ otherwise, the electrolytes can be oxidized and lead to safety issues. Therefore, for state-of-art cathode materials, the typical potentials of redox shuttles should be tunable from 3.8 V (for LiFePO₄ olivine) to 4.5 V [for LiMnO₄ or Li_{1.1}(Co_{1/3}Mn_{1/3}Ni_{1/3})_{0.9}O₂] vs. Li/Li⁺. However, with the high-voltage cathode materials and electrolytes recently emerging, redox shuttles with higher potentials (4.4 V to 4.9 V vs. Li/Li⁺) are also greatly needed.

Third, the electrochemical stability is of vital importance in determining the longevity of overcharge protection resulting from redox shuttles.^{20,21,23,28} This stability actually depends upon the stability of the oxidative species (S⁺ in Figure 1) of the redox shuttles generated during overcharge protection. However, evaluation of redox shuttle stability does not have a clear standard. Overcharge protection time and cycle numbers are mostly used to depict the overcharge longevity or stability. But considering most research uses various overcharge abuse test procedures and experimental setups to evaluate overcharge protection performance, it is difficult to compare redox shuttle performance from different research groups.²⁹ The variations of experimental details, such as cell types, amounts of electrolytes, formulation of electrolytes, concentrations of redox shuttles, charge rate, overcharge percentage, electrode loadings, electrode match-ups, use of other additives, and test temperatures, could all affect the evaluation results. To compare different redox shuttles, parallel tests under identical conditions have to be undertaken.

Finally, some other factors, such as a good solubility^{19,30} and high diffusion coefficient of the redox shuttles in non-aqueous electrolytes, are also highly desired to maximize the shuttle molecule's mobility through the cell, therefore delivering high-current overcharge protection.

These aforementioned characteristics allow targeting the development of redox shuttle additives with superior overcharge protection; however, besides overcharge, the normal cell performance resulting from the addition of redox shuttles has rarely been investigated and evaluated. Actually, the normal cell performance is of equal, if not greater, importance compared with the overcharge performance. After all, it is the merits of the normal cell performance that enables application of lithium-ion technology to various power sources.

The effect of redox shuttle additives on normal cell performance, or the so-called "compatibility" to the cell system, should be carefully evaluated and established as standards for ideal redox shuttles.²⁸ The compatibility can be determined for many different properties relative to different cell components. For instance, for the compatibility of the redox shuttle to the electrolyte solutions, the effects of redox shuttle solubility, conductivity, co-reaction, etc., have to be investigated and considered. For compatibility to electrode materials, the effects of the solid-electrolyte interface, interface resistance, co-reaction, and thermal property should be taken into account. As for the compatibility to other cell components, such as separators, current collectors, and binders, more studies may be needed to explore and set up standards for better redox shuttles. The characteristics regarding an ideal redox shuttle are summarized in Table 1 with respect to both overcharge protection and cell compatibility.

<i>Overcharge performance factors</i>	<i>Cell compatibility factors</i>
Electrochemical reversibility	Solubility in electrolytes
Redox potential	Effect on self-discharge
Electrochemical stability	Effect on conductivity
Molecular weight	Effect on impedance
Diffusion coefficient	Reactivity with cell components

Table 1. Characteristics for an ideal redox shuttle

4. Theoretical studies of redox shuttles

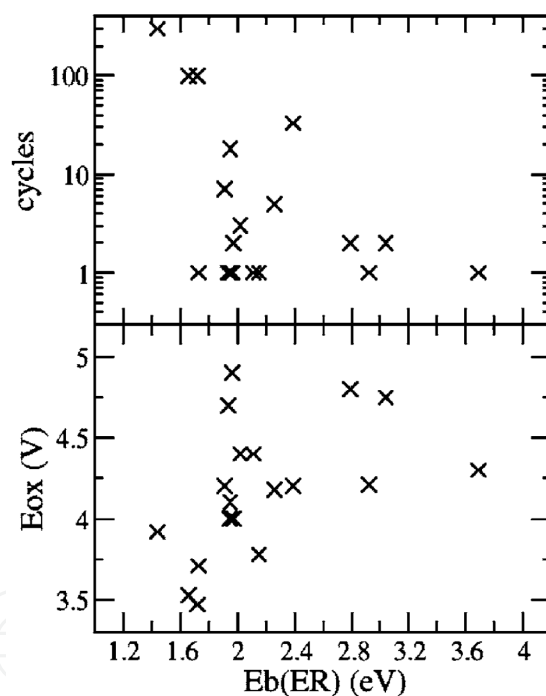
Development of redox shuttles with superior performance and excellent compatibility is of great importance to the lithium-ion battery technology. Various theoretical studies have been conducted to establish an efficient screening procedure for redox shuttles, including calculation of oxidation potentials³¹ and estimation of electrochemical stability.²¹ However, most theoretical results have been used to support experimental results and provide design guidance for development of novel redox shuttles. With few exceptions, the development of redox shuttle additives has been based on trial and error or experience. Reports on redox shuttles rarely state the design thinking or strategy that could help to build redox shuttles with tunable properties, such as potentials, electrochemical stabilities. A possible reason is that the redox shuttle design requires multi-discipline knowledge, including not only electrochemistry and lithium-ion battery technology, but also physical organic chemistry

and organic synthesis. For example, researchers with electrochemical knowledge and battery experience may understand the requirements of redox shuttles, but owing to a lack of knowledge about organic chemistry, would encounter serious impediments to practical design of a new system.

As one of the pioneering groups, Dahn and co-workers did some systematic work to calculate the relation between chemical structure and redox potential.³¹ The oxidation potentials of seventeen molecules used as candidate shuttle additives in Li-ion cells were calculated by density functional theory, and the results compared with experiment. Based on the correlation between the highest occupied molecular orbital (HOMO) energy and the oxidation potential, a good empirical relation was established (shown in equation 1), which can be used as a quick estimate of the oxidation potential for novel molecules:

$$E_{\text{est}}(\varepsilon) = -(\varepsilon/e) - 1.46 \text{ V} \quad (1)$$

where ε is the orbital energy in solution, in electron volts, and represents the energies of the molecule's HOMO; e is the electron charge; and $E_{\text{est}}(\varepsilon)$ is the estimated oxidation potential, in volts, relative to a Li/Li⁺ reference electrode.



$E_b(ER)$, the more stable the redox shuttle. The calculated binding energies of 19 selected oxidized shuttle molecules were found to agree approximately with the experimentally measured stability. Even though this method still has some limitations and inconsistencies, for the first time, it provided a quick evaluation to predict redox shuttle stability.

The computation prediction method for the redox potential and stability of redox shuttles was applied to *tert*-butyl- and methoxy-substituted benzene derivatives,³² which were chosen because of the earlier success of DDB. Both the oxidation potential and the stability of *tert*-butyl- and methoxy-substituted benzene molecules agreed well with the calculated results. Of the 43 molecules evaluated, DDB proved to be the most stable shuttle molecule suitable for LiFePO₄-based cells.

Chen and co-workers used molecular orbital theory to explain the stability of redox shuttles.²⁰ Their theoretical calculations clearly demonstrated that the π - π interaction between the aromatic ring and the substitution groups is critical to maximize the stability of radical cations. They also proposed that intermolecular polymerization is the major decomposing pathway, and that this source of instability can be minimized by full substitution on the aromatic ring.

Aromatic theory was later applied to explain the stability of the dimethoxybenzene system.¹ Aromaticity is a chemical property in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibits stabilization stronger than would be expected by the stabilization of the conjugation alone. It can also be considered a manifestation of cyclic delocalization and resonance.³³ A cyclic ring molecule follows Hückel's rule when the number of its π -electrons equals $4n+2$; where n is zero or any positive integer, the molecule can be regarded as an aromatic system. In the case of dimethoxybenzene, the lone pairs of the two oxygen atoms can participate in the conjugated benzene π -electrons, making 10 delocalized electrons and thus forming a large stable conjugated system. This process partially explains the excellent stability of DDB. The *tert*-butyl groups in DDB also play an important role in stabilizing the radical cation.¹⁷ The steric hindrance effects prevent the active radical cation from intermolecular annihilation, leading to enhanced longevity of overcharge protection.

5. Rational design of redox shuttles with tunable properties

5.1 Overcharge protection performance

For an ideal redox shuttle, the desirable additive needs to be tunable with regard to many properties (Table 1), to accommodate different cell chemistries, and to resolve issues that not only could occur during overcharge protection, but also during normal operation. For instance, to minimize the self-discharge effect for different cathode materials, tunable redox potentials are desired and, ideally, should be 0.3~0.4 V higher than the end-of-charge potential. The electrochemical stability is also important when designing a redox shuttle; therefore, factors like electron donating effect or steric hindrance should be considered.

In 2005 Caudia et al. developed DDB (**10** in Figure 2) on the basis of a screening selection,³⁴ and this molecule stood out as possessing many unique and desirable features. It is built on the benzene ring with two methoxy groups helping to stabilize the radical cation that could be produced during the overcharge process, and two *tert*-butyl groups were attached to the benzene ring to protect the radical cation from intermolecular annihilation.^{20,28} With this

design, DDB displays perfect electrochemical reversibility at 3.9 V *vs.* Li/Li⁺ and provides over 200 cycles of overcharge protection to the lithium-ion cells using LiFePO₄ cathodes. DDB meets most of the aforementioned characteristics in terms of overcharge performance and is very close to practical application. DDB has a simple chemical structure, leaving ample room for organic modification. In addition, the benzene ring is known as the smallest hydrocarbon conjugated system with the least electron density so that, compared with other heterocyclic aromatic systems, it has the most chance to achieve high oxidation potential, a favorable feature for the design of novel redox shuttles. Therefore, DDB provides an excellent starting point from which to tune properties, such as redox potential, and cell compatibility.

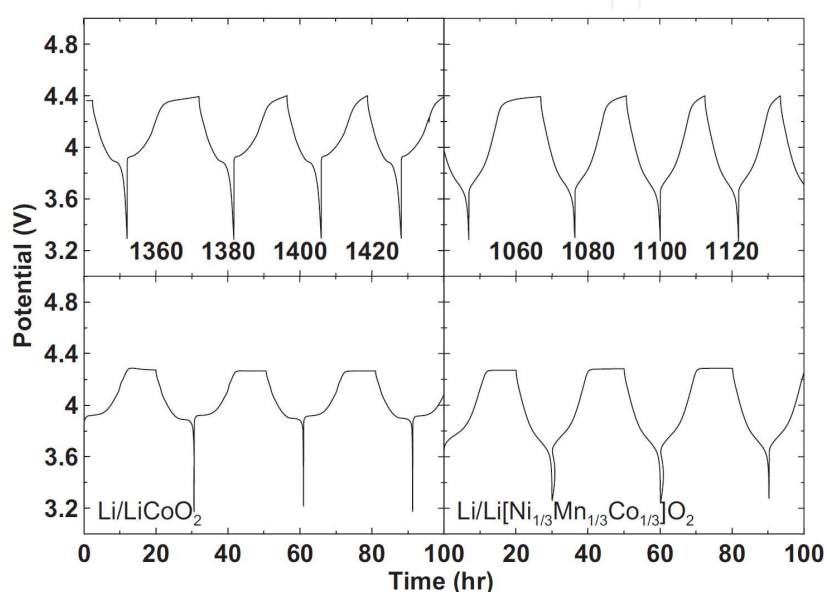


Fig. 4. Coin cell data for Li/LiCoO₂ cells (left) and Li/Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ cells (right) containing 0.1 M 1,4-di-*tert*-butyl-2,5-bis(2,2,2-trifluoroethoxy)benzene in an electrolyte composed of 0.5 M LiPF₆ in propylene carbonate (PC): dimethyl carbonate (DMC): ethylene carbonate (EC): diethyl carbonate (DEC) in a 1:2:1:2 ratio by volume. Cells were charged at C/10 rate for 20 h and then discharged at C/10 rate. (Reprinted from Journal of the Electrochemical Society, 2009, 156, A309., Copyright (2009), with permission from the Electrochemical Society.)

DDB is electrochemically reversible at 3.9 V, which is high enough for the LiFePO₄ cathode but not for 4-V class cathode materials. Therefore, increasing the redox shuttle of this molecule is of great importance. According to molecular orbital theory, increasing the oxidation potential means lowering the energy or electron density of the HOMO orbital.³⁵ A recent example was reported in 2009,²⁴ when the potential of 1,4-di-*tert*-butyl-2,5-bis(2,2,2-trifluoroethoxy)benzene (**15** in Figure 2) was increased to 4.25 V (*vs.* Li/Li⁺) by introducing electron-withdrawing trifluoroethyl groups. As shown in Figure 4, this new redox shuttle provided overcharge protection for Li/LiCoO₂ and Li/Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ cells for around 40 cycles. This report signified a promising direction for development of novel redox shuttles: that is, use of a DDB platform to retain the excellent electrochemical properties and introduction of electron withdrawing groups to raise the potential. However, because the incorporated trifluoroethyl groups are not directly attached to the conjugated ring, the resultant potential is still not very high, especially for the new high-energy 5-V materials.^{36,37}

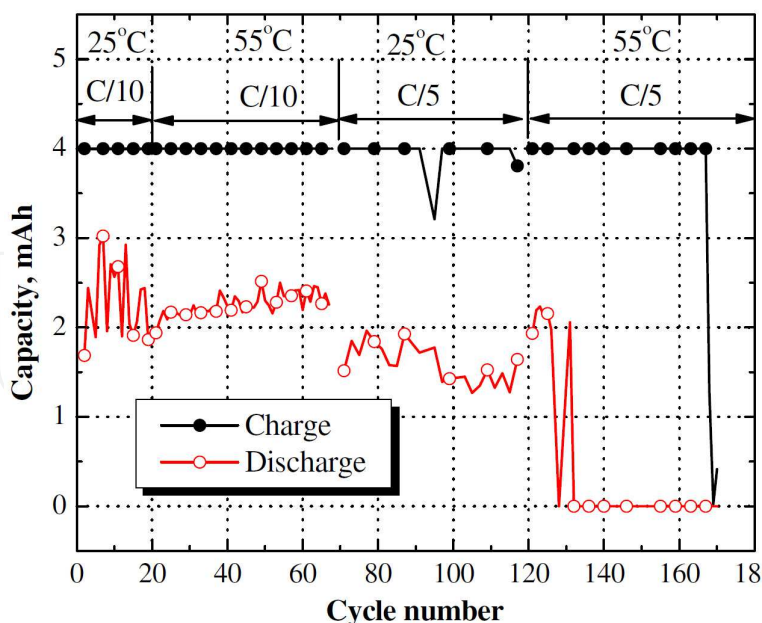


Fig. 5. Charge and discharge capacity of graphite/ $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cell during the whole course of overcharge test. The electrolyte used contained 5 wt% PFPTFBB. (Reprinted from *Electrochem. Commun.*, 9: 703–707, Copyright (2007), with permission from Elsevier).

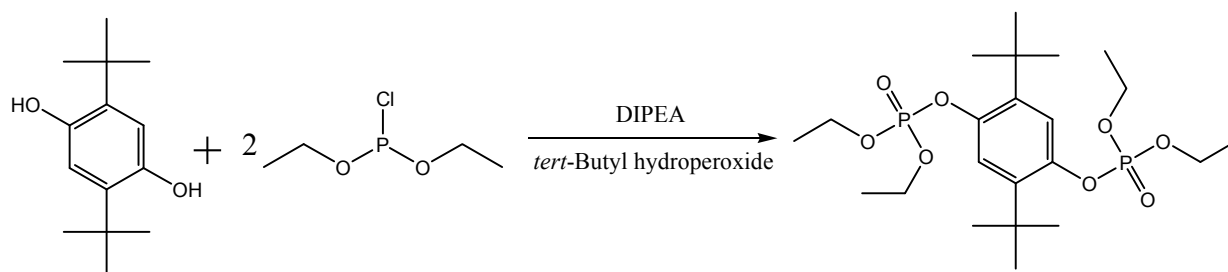


Fig. 6. Synthesis route of tetraethyl-2,5-di-*tert*-butyl-1,4-phenylene diphosphate (TEDBPDP).

Another promising molecule using fluorine groups to increase the redox potential is 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole (PFPTFBB) (**14** in Figure 2).²³ This shuttle is also based on the dimethoxybenzene platform, but the two methoxy groups are in the ortho positions. As shown in Figure 2, PFPTFBB was fully substituted by fluorine atoms. The fluorine atoms were directly attached to the conjugated ring and increased the reversible potential to 4.46 V vs. Li/Li^+ , high enough for most 4-V cathode materials. In addition, the fully substituted structure made this molecule stable against possible polymerization during the overcharge protection process; therefore, PFPTFBB can provide long-time overcharge protection. For instance, as shown in Figure 5, 5 wt% PFPTFBB in the electrolyte can provide more than 150 overcharge cycles, even under elevated temperature and at a high charge rate. However, this molecule is extremely difficult to synthesize and is not chemically stable against moisture.³⁸

Even though 1,4-di-*tert*-butyl-2,5-bis(2,2,2-trifluoroethoxy)benzene and PFPTFBB achieved increased oxidation potentials, the potentials of these shuttle molecules are still not high enough to be used for cathode materials with potentials higher than 4.4 V. With numerous high-voltage and high-energy cathode materials closer to application as a large-scale power source,^{36,37,39,40} the potential of the corresponding redox shuttle additives must be increased.

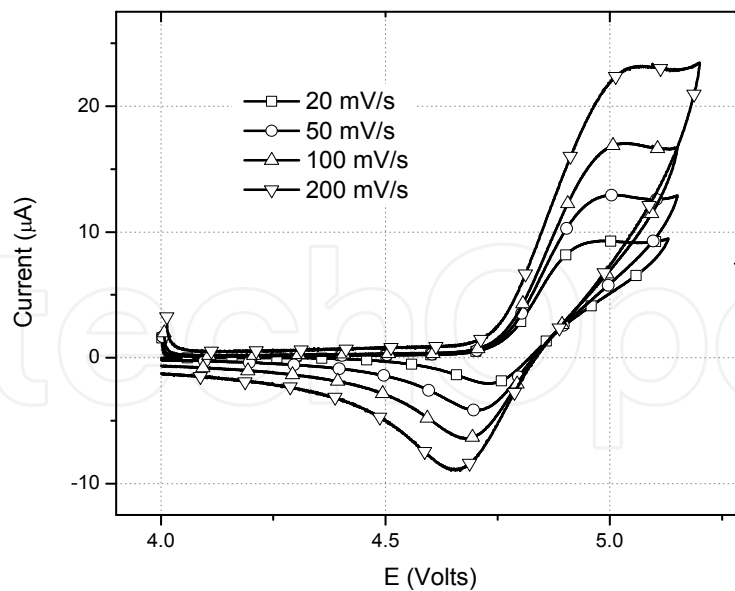


Fig. 7. Cyclic voltammogram of 1.2 M LiPF_6 in EC/DEC (3:7 by weight) with 0.01M TEDBPFP at various rates using a Pt/Li/Li three-electrode system.

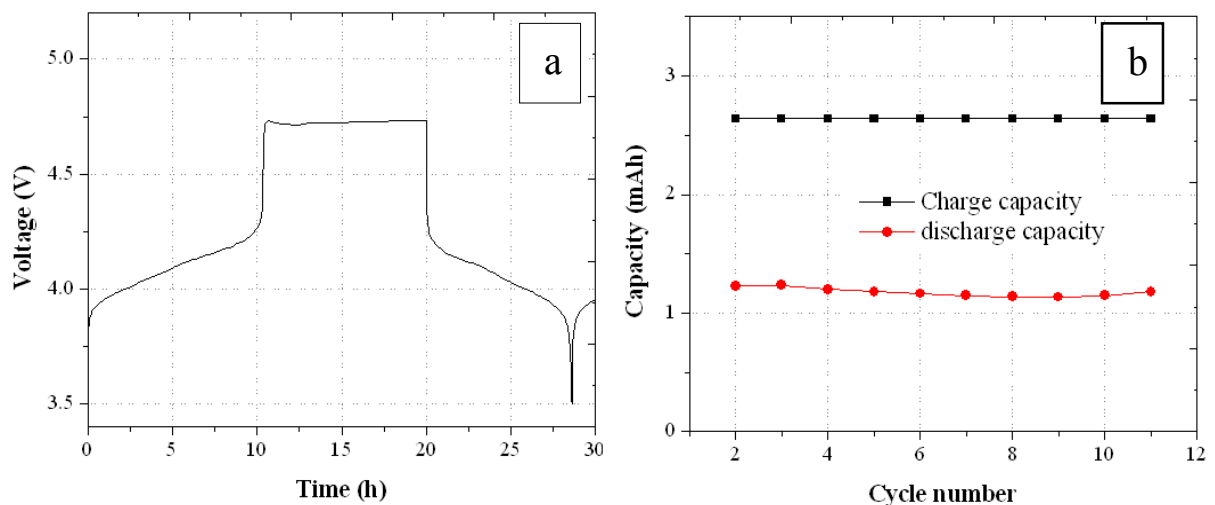


Fig. 8. a) Representative cell voltage *vs.* time for $\text{LiMn}_2\text{O}_4/\text{Li}$ cell containing 5 wt% TEDBPDP; b) cell charge-discharge capacities *vs.* cycle number in overcharge test. Cells were charged at C/10 rate for 20 h and then discharged at C/10 rate.

For example, a new high-energy cathode material developed at Argonne National Laboratory^{36,37} requires redox shuttle additives having potential higher than 4.9 V *vs.* Li/Li⁺. Recently, Zhang et al. at Argonne developed a novel organophosphate functionalized redox shuttle molecule, tetraethyl-2,5-di-*tert*-butyl-1,4-phenylene diphosphate (TEDBPDP), which can provide overcharge protection for high-voltage cathode materials.⁴¹ Figure 6 shows the reaction for the synthesis of TEDBPDP. The structure of TEDBPDP was also based upon the dimethoxybenzene ring platform. Instead of using fluorine atoms, however, organic phosphate groups were attached to the conjugated system to increase the redox potential. Belfield et al. had reported that organic phosphate groups are strong electron-withdrawing units in organic chemistry.⁴² In addition, organic phosphate compounds have been studied as flame retardant additives for lithium-ion batteries,⁴³⁻⁴⁷ bringing an additional benefit of

this novel redox shuttle. As shown in Figure 7, the redox potential of TEDBPDP, obtained from the mean of the anodic and cathodic potentials $((E_a + E_c)/2)$, is 4.80 V *vs.* Li/Li⁺, indicating the strong effect of the incorporated organic phosphate groups. To the best of our knowledge, 4.80 V is the highest redox shuttle potential ever reported in the literature. The oxidation potential of TEDBPDP is high enough for most >4.2 V cathode materials.

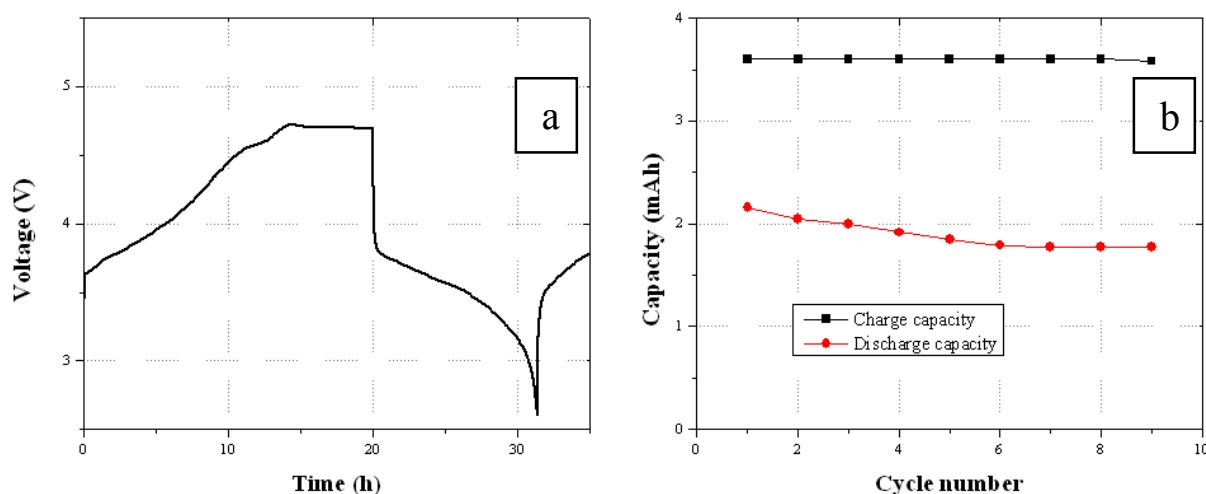


Fig. 9. a) Representative cell voltage *vs.* time for Li/Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O₂ cell containing 5 wt% TEDBPDP; b) cell charge-discharge capacities *vs.* cycle number in overcharge test. Cells were charged at C/10 rate for 20 h and then discharged at C/10 rate.

Figure 8 shows the overcharge performance of Li/LiMn₂O₄ cells containing 5 wt% TEDBPDP in the 1.2 M LiPF₆ electrolyte. As indicated by Figure 8(a), during the charge, lithium ion was removed from the LiMn₂O₄ cathode and reduced on the Li metal anode. The normal charge took place at about 3.9–4.3 V. After the cell was fully charged, the voltage climbed up quickly to 4.75 V, where the redox shuttle was activated. The flat plateau at 4.75 V indicates that the overcharge current was manipulated by the TEDBPDP molecules. At 100% overcharge, the amount of overcharge can be further increased, and TEDBPDP can provide more than 10 cycles of overcharge protection before the shuttle molecule becomes ineffective, as illustrated in Figure 8(b).

Figure 9 shows the results from an overcharge test using a Li/Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O₂ cell containing 5 wt% TEDBPDP in the electrolyte. This cathode required formation cycles between 2.8 V and 4.6 V before the overcharge tests. As shown in Figure 9(a), the normal charge took place starting at about 3.7 V and continued until the voltage reached 4.75 V, where the redox shuttle mechanism was activated. Even though the cell was not in an overcharge state due to the high cut-off working potential of this cathode material, the plateau at 4.75 V is a clear indication of the TEDBPDP overcharge protection. As indicated by Figure 9(b), the average capacities for charge are nearly twice those of discharge. The results demonstrate a successful example for using TEDBPDP to provide overcharge protection for a high potential cathode.

5.2 Cell compatibility

Another direction for redox shuttle improvement involves compatibility with the lithium-ion cell system. Take DDB as an example. It excels at overcharge performance in terms of suitable

potential for LiFePO_4 , length of overcharge protection, etc. However, DDB is not quite compatible with the lithium-ion cell system; specifically, it is not soluble with the conventional carbonate-based electrolytes.⁴⁸ For instance, in an electrolyte of 1.2 M LiPF_6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a weight ratio of 3:7 (Gen 2 electrolyte), DDB can dissolve up to only 0.08 M, which is not enough in most cases. The literature studies on this molecule for overcharge protection of lithium-ion batteries mostly employ a special formulated electrolyte with reduced lithium salt concentration, such as 0.5 M lithium bis(oxalato)borate (LiBOB) in propylene carbonate (PC): dimethyl carbonate (DEC) at a volume ratio of 1:2.^{34,48-50} This different formulation of the electrolyte sacrifices cell performance due to a lower conductivity, which is not acceptable for the battery industry.

Quite a few strategies have been pursued to improve the dimethoxybenzene-based redox shuttle.^{28,30,51-53} For instance, to improve the solubility of DDB in carbonate-based electrolyte, Zhang et al. at Argonne²⁸ and others³⁰ have investigated an asymmetric structure design (ANL-1 in Figure 10) to create intramolecular dipole moments that facilitate the dissolution of the redox shuttle in the electrolyte. However, while successful in improving solubility, those asymmetric redox shuttles appear to be less electrochemically stable because the electronic structure of the redox center is disturbed and certain chemical bonds are weakened within the structure, which, as a result, does not provide long enough overcharge protection.

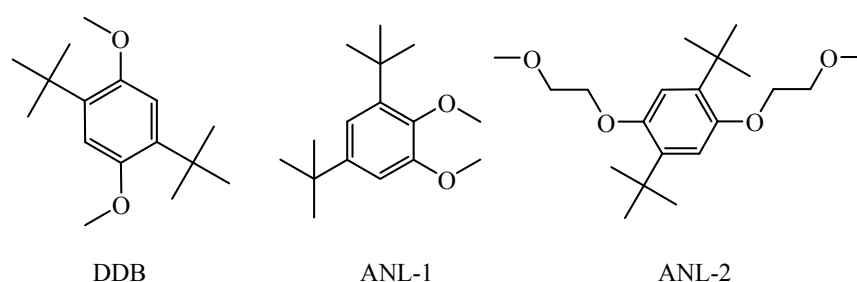


Fig. 10. Chemical structures of dimethoxybenzene-based redox shuttles

Recently, a new strategy was adopted to develop a novel redox shuttle (ANL-2) that is not only soluble in carbonate-based electrolyte but also retains the excellent overcharge performance of DDB.⁵⁴⁻⁵⁶ ANL-2 was developed by introducing oligo ether groups, such as oligo(ethylene glycol) (OEG), into the symmetric dimethoxy-di-*tert*-benzene platform. Oligo ether groups contain repeating ether units, which are well known to be soluble in polar solutions, such as water. The introduction of OEG into the redox shuttle structure significantly improved the solubility in polar carbonate electrolytes. For instance, ANL-2 redox shuttle can dissolve in Gen 2 electrolyte up to 0.4 M. More important, the modification does not break the symmetric structures of the molecules and, therefore, maintains the essential electrochemical properties.

Figure 11 shows voltage profiles of mesocarbon microbead (MCMB)/ LiFePO_4 cells containing 0.4 M ANL-2 in Gen 2 electrolyte during 960 hours of an overcharge test. The charge rate was set to $C/2$, which is identical or even greater than the practical charge rate for lithium-ion batteries. Under this aggressive condition, the ANL-2 redox shuttle still worked well and provided around one-thousand hours of overcharge protection, which is more than 180 cycles (see Figure 12). This is the first redox shuttle ever reported that can work well in Gen 2 electrolyte and provide more than 180 cycles at an overcharge ratio of 100% and $C/2$ charge rate. Compared with DDB, the ANL-2 redox shuttle has comparable

overcharge protection performance but much improved solubility in carbonate-based electrolytes, making it more applicable to lithium-ion batteries.

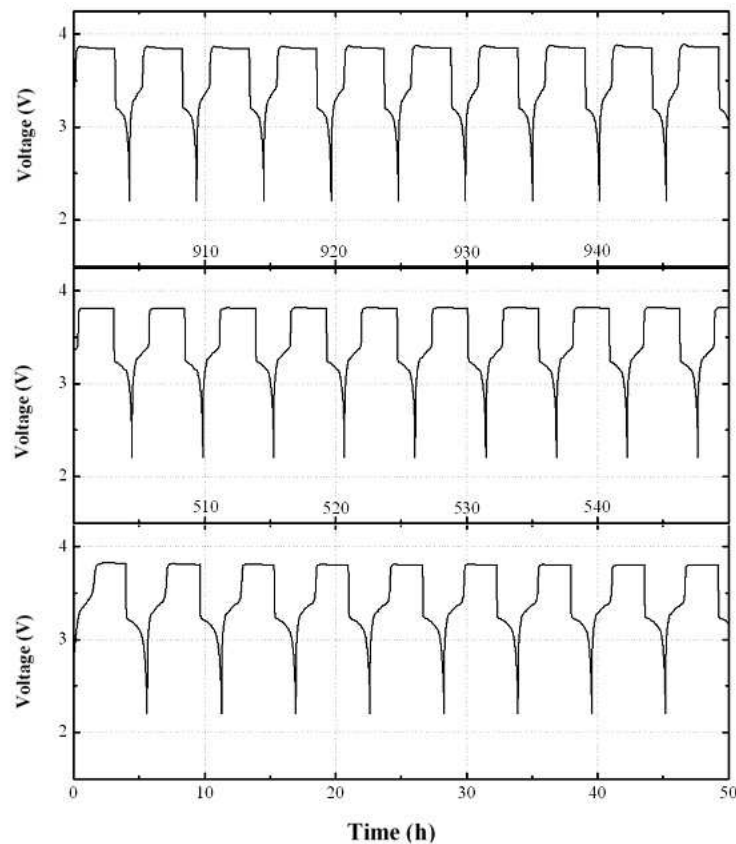


Fig. 11. Voltage profiles of MCMB/LiFePO₄ cells containing 0.4 M ANL-2 in Gen 2 electrolyte during 960-h overcharge test. Charging rate is C/2, and overcharge ratio is 100%.

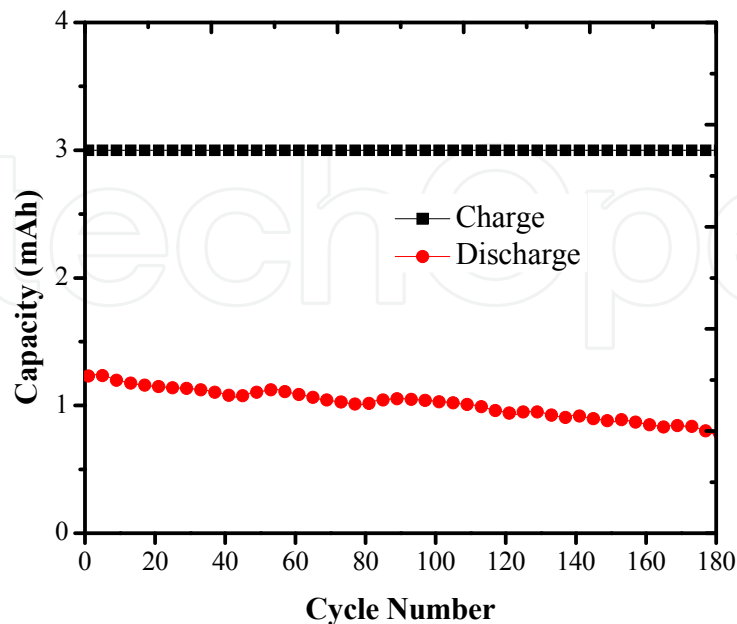


Fig. 12. Capacity retention profiles of MCMB/LiFePO₄ containing 0.4 M ANL-2 in Gen 2 electrolyte. Charging rate is C/2, and overcharge ratio is 100%.

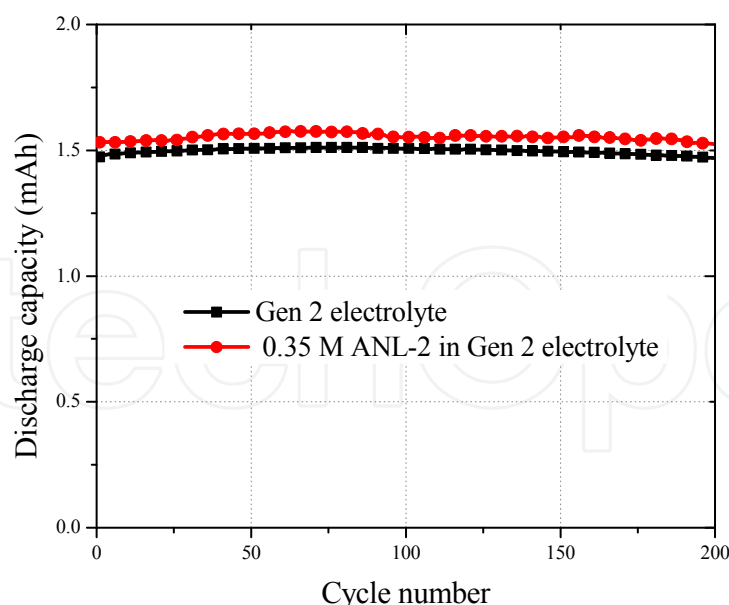


Fig. 13. Capacity retention profiles of MCMB/LiFePO₄ cells containing Gen 2 electrolyte with and without 0.35 M ANL-2 additive. Charging rate is C/3, and cut-off voltage is 2.3 ~3.6 V.

Figure 13 shows the discharge capacity retention of MCMB/LiFePO₄ cells containing Gen 2 electrolyte with and without 0.35 M ANL-2. The charge rate is set to C/3, and cut-off voltages are 2.3~3.6 V. As shown in Figure 13, the discharge capacity retention profiles for the cells with the two different electrolytes are similar, indicating that the ANL-2 additive does not degrade cell performance. This is the first redox shuttle example ever reported in the literature that not only excels at overcharge protection but also is compatible with state-of-art lithium-ion cell components. The ANL-2 redox shuttle could thus be used directly in current lithium-ion batteries.

6. Conclusion

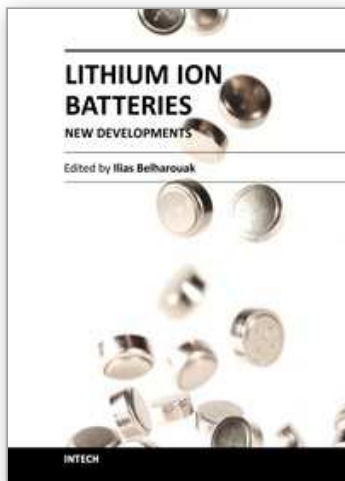
Redox shuttle additives have been extensively studied due to their unique features and promising applications in lithium-ion batteries. This review of the literature covers their intrinsic chemical overcharge protection mechanism as determined by both theoretical and experimental studies, the correlation between chemical structure and overcharge performance, and development of novel redox shuttles with tunable properties that are related to overcharge performance and normal cycle performance.

7. References

- [1] Chen, Z.; Qin, Y.; Amine, K. *Electrochimica Acta* 2009, 54, 5605.
- [2] Zhang, S. S. *Journal of Power Sources* 2006, 162, 1379.
- [3] Zhang, Z. C.; Zhang, L.; Schlueter, J. A.; Redfern, P. C.; Curtiss, L.; Amine, K. *Journal of Power Sources* 2010, 195, 4957.
- [4] Abraham, K. M.; Pasquariello, D. M.; Willstaedt, E. B. In *Journal of the Electrochemical Society* Journal of the Electrochemical Society 1990; Vol. 137, p 1856.
- [5] Jonsson, M.; Lind, J.; Reitberger, T.; Eriksen, T. E.; Merenyi, G. *The Journal of Physical Chemistry* 1993, 97, 11278.

- [6] Golovin, M. N.; Wilkinson, D. P.; Dudley, J. T.; Holonko, D.; Woo, S. *Journal of The Electrochemical Society* 1992, 139, 5.
- [7] Thomas, J. R.; Philip N. Ross, Jr. *Journal of The Electrochemical Society* 1996, 143, 3992.
- [8] Demmano, G.; Selegny, E.; Vincent, J. C. *Bioelectroch Bioener* 1996, 40, 239.
- [9] Behl, W. K.; Chin, D.-T. *Journal of The Electrochemical Society* 1988, 135, 16.
- [10] Behl, W. K.; Chin, D.-T. *Journal of The Electrochemical Society* 1988, 135, 21.
- [11] Behl, W. K. *Journal of The Electrochemical Society* 1989, 136, 2305.
- [12] Abraham, K. M.; Pasquariello, D. M.; Willstaedt, E. B.; 6 ed.; ECS: 1990; Vol. 137, p 1856.
- [13] Stepnicka, P. *Ferrocenes : ligands, materials and biomolecules*; J.Wiley: Chichester, England; Hoboken, NJ, 2008.
- [14] Tran-Van, F.; Provencher, M.; Choquette, Y.; Delabouglise, D. *Electrochimica Acta* 1999, 44, 2789.
- [15] Adachi, M.; Tanaka, K.; Sekai, K. *Journal of the Electrochemical Society* 1999, 146, 1256.
- [16] Lee, D. Y.; Lee, H. S.; Kim, H. S.; Sun, H. Y.; Seung, D. Y. *Korean J Chem Eng* 2002, 19, 645.
- [17] Chen, J.; Buhrmester, C.; Dahn, J. R. *Electrochemical and Solid-State Letters* 2005, 8, A59.
- [18] Moshurchak, L. M.; Buhrmester, C.; Dahn, J. R. *Journal of the Electrochemical Society* 2005, 152, A1279.
- [19] Dahn, J. R.; Jiang, J. W.; Moshurchak, L. M.; Fleischauer, M. D.; Buhrmester, C.; Krause, L. J. *Journal of the Electrochemical Society* 2005, 152, A1283.
- [20] Chen, Z.; Wang, Q.; Khalil, A. *Journal of The Electrochemical Society* 2006, 153, A2215.
- [21] Wang, R. L.; Dahn, J. R. *Journal of the Electrochemical Society* 2006, 153, A1922.
- [22] Moshurchak, L. M.; Buhrmester, C.; Dahn, J. R. *Journal of the Electrochemical Society* 2008, 155, A129.
- [23] Chen, Z.; Amine, K. *Electrochemistry Communications* 2007, 9, 703.
- [24] Moshurchak, L. M.; Lamanna, W. M.; Bulinski, M.; Wang, R. L.; Garsuch, R. R.; Jiang, J. W.; Magnuson, D.; Triemert, M.; Dahn, J. R. *Journal of the Electrochemical Society* 2009, 156, A309.
- [25] Chen, Z.; Liu, J.; Jansen, N. A.; GirishKumar, G.; Casteel, B.; Amine, K. *Electrochemical and Solid-State Letters* 2010, 13, A39.
- [26] Narayanan, S. R.; Surampudi, S.; Attia, A. I.; Bankston, C. P. *Journal of The Electrochemical Society* 1991, 138, 2224.
- [27] Xu, K. *Chemical Reviews* 2004, 104, 4303.
- [28] Zhang, Z.; Zhang, L.; Schlueter, J. A.; Redfern, P. C.; Curtiss, L.; Amine, K. *Journal of Power Sources* 2010, 195, 4957.
- [29] Moshuchak, L. M.; Bulinski, M.; Lamanna, W. M.; Wang, R. L.; Dahn, J. R. *Electrochemistry Communications* 2007, 9, 1497.
- [30] Feng, J. K.; Ai, X. P.; Cao, Y. L.; Yang, H. X. *Electrochemistry Communications* 2007, 9, 25.
- [31] Wang, R. L.; Buhrmester, C.; Dahn, J. R. *Journal of the Electrochemical Society* 2006, 153, A445.
- [32] Wang, R. L.; Moshurchak, L. M.; Lamanna, W. M.; Bulinski, M.; Dahn, J. R. *Journal of The Electrochemical Society* 2008, 155, A66.
- [33] Schleyer, P. v. R. *Chemical Reviews* 2001, 101, 1115.
- [34] Claudia, B.; Jun, C.; Lee, M.; Junwei, J.; Richard Liangchen, W.; Dahn, J. R. *Journal of The Electrochemical Society* 2005, 152, A2390.
- [35] Goodenough, J. B.; Kim, Y. *Chemistry of Materials* 2009, 22, 587.

- [36] Deng, H.; Belharouak, I.; Sun, Y.-K.; Amine, K. *Journal of Materials Chemistry* 2009, 19, 4510.
- [37] Deng, H.; Belharouak, I.; Wu, H.; Dambournet, D.; Amine, K. *Journal of The Electrochemical Society* 2010, 157, A776.
- [38] Weng, W.; Zhang, Z.; Schlueter, J. A.; Redfern, P. C.; Curtiss, L. A.; Amine, K. *Journal of Power Sources* 2011, 196, 2171.
- [39] Park, S. H.; Kang, S. H.; Johnson, C. S.; Amine, K.; Thackeray, M. M. *Electrochemistry Communications* 2007, 9, 262.
- [40] Sun, Y.-K.; Myung, S.-T.; Park, B.-C.; Prakash, J.; Belharouak, I.; Amine, K. *Nat Mater* 2009, 8, 320.
- [41] Zhang, L.; Zhang, Z.; Wu, H.; Amine, K. *Energy & Environmental Science* 2011.
- [42] Belfield, K. D.; Chinna, C.; Schafer, K. J. *Tetrahedron Letters* 1997, 38, 6131.
- [43] Xiang, H. F.; Xu, H. Y.; Wang, Z. Z.; Chen, C. H. *Journal of Power Sources* 2007, 173, 562.
- [44] Izquierdo-Gonzales, S.; Li, W.; Lucht, B. L. *Journal of Power Sources* 2004, 135, 291.
- [45] Xu, K.; Zhang, S.; Allen, J. L.; Jow, T. R. *Journal of The Electrochemical Society* 2002, 149, A1079.
- [46] Ma, Y.; Yin, G.; Zuo, P.; Tan, X.; Gao, Y.; Shi, P. *Electrochemical and Solid-State Letters* 2008, 11, A129.
- [47] Feng, J. K.; Cao, Y. L.; Ai, X. P.; Yang, H. X. *Electrochimica Acta* 2008, 53, 8265.
- [48] Dahn, J. R.; Junwei, J.; Moshurchak, L. M.; Fleischauer, M. D.; Buhrmester, C.; Krause, L. J. *Journal of The Electrochemical Society* 2005, 152, A1283.
- [49] Moshurchak, L. M.; Buhrmester, C.; Dahn, J. R. *Journal of The Electrochemical Society* 2005, 152, A1279.
- [50] Jun, C.; Claudia, B.; Dahn, J. R. *Electrochemical and Solid-State Letters* 2005, 8, A59.
- [51] Weng, W.; Zhang, Z.; Redfern, P. C.; Curtiss, L. A.; Amine, K. *Journal of Power Sources* 2010, 196, 1530.
- [52] Moshurchak, L. M.; Lamanna, W. M.; Mike, B.; Wang, R. L.; Rita, R. G.; Junwei, J.; Magnuson, D.; Matthew, T.; Dahn, J. R. *Journal of The Electrochemical Society* 2009, 156, A309.
- [53] Weng, W.; Zhang, Z.; Schlueter, J. A.; Redfern, P. C.; Curtiss, L. A.; Amine, K. *Journal of Power Sources* 2010, 196, 2171.
- [54] Amine, K.; Zhang, L.; Zhang, Z.; DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING. 2011.
- [55] Krumdick, G. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING 2011.
- [56] Zhang, L.; Zhang, Z.; Amine, K. *unpublished* 2011.



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The eight chapters in this book cover topics on advanced anode and cathode materials, materials design, materials screening, electrode architectures, diagnostics and materials characterization, and electrode/electrolyte interface characterization for lithium batteries. All these topics were carefully chosen to reflect the most recent advances in the science and technology of rechargeable Li-ion batteries, to provide wide readership with a platform of subjects that will help in the understanding of current technologies, and to shed light on areas of deficiency and to energize prospects for future advances.

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