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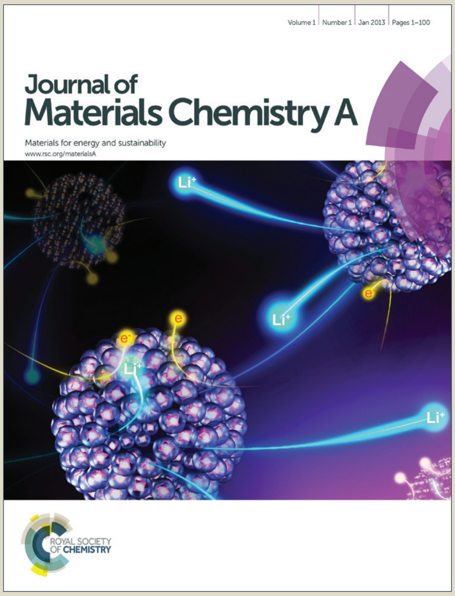

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The Organophosphine Oxide Redox Shuttle Additive That Delivers Long-term Overcharge Protection in 4 V Lithium-ion Batteries

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Redox shuttle additives are used to protect Li-ion batteries from overcharge. Increased operation voltage requires striking a balance between a high redox potential and electrochemical stability. 1,4-Bis[bis(1-methylethyl)phosphinyl]-2,5-dimethoxybenzene (BPDB) exhibits a redox potential of 4.5 V *vs*. Li/Li$^+$ and provides stable overcharge protection for 4 V cells delivering 95 cycles of 100% overcharge ratio.

Rechargeable lithium-ion batteries (LIBs) are ubiquitous in portable electronic devices and are being extensively pursued for transportation applications, including hybrid electric vehicles due to their unique features such as high energy density, low self-discharge, long cycle life, no memory effect, wide operation temperature, and fairly high rate capability.[1, 2] However, safety concerns have plagued wider commercial applications of LIBs.[3] In particular, overcharge abuse is considered as one of the most common and dangerous safety issues. Overcharge is a condition where the electricity flow is forced through a cell after reaching its full capacity and consequently raises the potential beyond the electrochemical window of the electrolyte, leading to solvent breakdown, thermal runaway and even explosion.[4, 5] Several methods have been proposed to prevent these adverse processes,[5] including voltage monitoring electronic devices attached to each individual cell in a battery pack, and utilization of electrolyte additives. Compared with the external electronic devices, the electrolyte additives, such as the redox shuttle additives, have been considered to be a more economical option.[5]

Generally, the shuttle molecule exhibits reversible redox reaction with a defined potential that is slightly higher (≥ 0.3 V) than the end-of-charge potential of the cathode. When the cell enters the overcharge condition, the cell voltage increases until it reaches the potential of the redox shuttle. The molecule is oxidized at the cathode surface to form a radical cation, which diffuses to the anode surface, becomes reduced, and then diffuses back to the cathode to initiate the next oxidation/reduction cycle. This cycle becomes a molecular short circuit that mitigates overcharge abuse. The voltage of the cell is locked by the redox potential of the redox shuttle, thereby minimizing chemical deterioration of LIBs.[6, 7]

Many classes of organic molecules have been examined as redox shuttle candidates, which can be categorized based on their redox platforms, including such common choices as ferrocene,[8, 9] 2,2,6,6-tetramethylpiperinyl-oxide,[10] phenothiazine,[11-14] and dimethoxybenzene.[6, 15-18] Dimethoxybenzene derivatives were first investigated by Adachi and coworkers,[16] and are increasingly popular due to their promising electrochemical behavior, tuneable electronic properties, and the ease of synthetic variation. Dahn and co-workers have shown that 2,5-di-*tert*-butyl-1,4-dimethoxybenzene (DDB, Figure 1)[6, 19] exhibits exceptionally robust overcharge protection. DDB is oxidized at 3.9 V *vs*. Li/Li$^+$, and it can provide over 300 cycles of 100% overcharge per cycle for Li-ion cells with $LiFePO_4$ cathode. Despite these advantages, DDB also has limitations, including relatively low solubility in the carbonate electrolyte and the redox potential that is insufficient for 4 V operation of LIBs. With numerous high-voltage and high-energy cathode materials currently being examined, the redox potential of the shuttle additives needs to increase.

Several dimethoxybenzene derivatives with the increased redox potentials have been developed, such as 1,4-di-*tert*-butyl-2,5-bis(2,2,2-trifluoroethoxy)benzene (DBTFB) and tetraethyl-2,5-di-*tert*-butyl-1,4-phenylene diphosphate (TEDBPDP) that are shown in Figure 1.[20-22] The general approach has been to incorporate electron withdrawing groups into the benzene ring, so that the HOMO energy becomes lowered due to the reduced electron density. However, this modification is not favorable for stabilization of the radical cations that are generated during overcharge, which adversely impacts the electrochemical stability of the shuttle molecules. This adverse tendency is exemplified by DBTFB and TEDBPDP shown in Figure 1. DBTFB has two trifluoroethoxy electron withdrawing groups and a redox potential at 4.25 V *vs*. Li/Li$^+$. While it is structurally similar to DDB, it is considerably less stable.[6, 20] In TEDBPDP, the strong electron withdrawing effect of the two organophosphate groups yields the highest redox potential reported for a functional redox shuttle in the literature, that is 4.75 V *vs.* Li/Li$^+$,[21] yet this additive exhibits only 10 protection cycles for the cells with $LiMn_2O_4$ (LMO) and $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ cathodes indicating poor electrochemical stability. Not only the radical cations of such high-potential redox shuttle molecules become more energetic and reactive, causing undesired side reactions, but these molecules themselves (due to the presence of these electron withdrawing groups) become more vulnerable to anode reduction, compounding the problem.

This dilemma of high redox potential *vs.* low electrochemical stability poses a formidable challenge for development of protective "molecular circuits" suitable for 4 V LIBs. Herein we show a way out of this predicament through the use of organophospine oxide modification of the dimethoxybenzene (Figure 1). These two molecules (BPDB and BPDFDB) were synthesized following procedures outlined in the Supporting Information.[23, 24] The organophosphine oxide groups exhibit strong electron withdrawing properties.[25] Due to their rigid tetrahedral structure, they also provide excellent steric protection of the electrochemically generated radical cation against recombination and addition. The fluorine atoms in BPDFDB were expected to further increase the redox potential.[26]

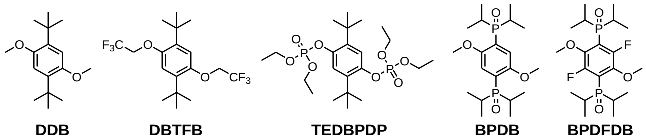

Figure 1**.** Chemical structures for dimethoxybenzene based redox shuttles.

The electrochemical reversibility of these redox shuttle molecules was evaluated using cyclic voltammetry. Cyclic voltammograms of BPDB and BPDFDB were obtained in Gen 2 electrolyte (1.2 M $LiPF_6$ in 3:7 wt/wt mixture of ethylene carbonate and ethyl methyl carbonate) using a Pt/Li/Li three-electrode system. As seen in Figure 2, BPDB displays a well-defined reversible redox wave corresponding to 4.5 V *vs.* Li/Li$^+$, which can be compared to 3.9 V *vs.* Li/Li$^+$ for DDB. In contrast, the oxidation of BPDFDB was not electrochemically reversible. The oxidation and reduction peaks are separated (at 5.0 and 4.3 V, respectively) and the area of the oxidation peak is considerably greater than the area of the reduction peak. Such irreversibility excludes the use of this molecule as a redox shuttle.

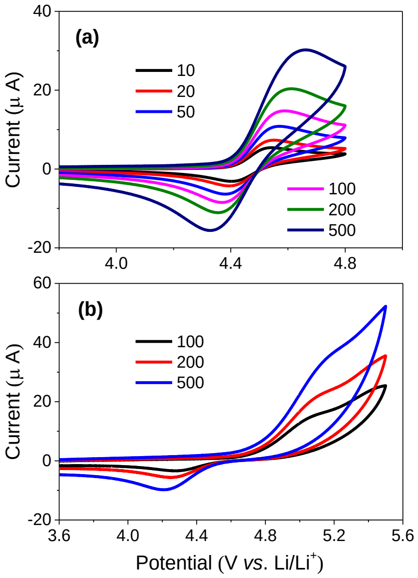

Figure 2**.** Cyclic voltammograms of 0.01 M BPDB (a) and BPDFDB (b) in Gen 2 electrolyte at various scan rates (mV/s) in a Pt/Li/Li three-electrode system.

Since BPDB was electrochemically reversible, it was further evaluated. The high redox potential of this molecule makes it suitable for overcharge protection of 4 V cathode materials, such as spinel LMO,[27] that is widely used in the commercial LIBs. Lately, LMO has also been investigated as a promising cathode candidate for LIBs in hybrid electric vehicles due to its low cost, non-toxicity, high electrolyte compatibility and excellent power capability.[28] The end-of-charge potential of LMO is 4.2 V *vs.* Li/Li$^+$, which is 0.3 V lower than the redox potential of BPDB. We also note that the solubility of BPDB in Gen 2 electrolyte at room temperature exceeds 10 wt% (0.3 M), which is more than sufficient for the practical application.

Figure 3 exhibits voltage and capacity retention profiles of mesocarbon microbead (MCMB)/LMO cells containing 5 wt% (0.15 M) BPDB in Gen 2 electrolyte during overcharge cycling. The cells were first charged at C/10 rate for 20 h to make 100% overcharge (i.e., overcharge capacity/normal charge capacity equals 1), and then were discharged at C/10 rate to 3.0 V. As indicated in Figure 3a, for each cycle, the first plateau occurred at 3.0-4.1 V representing the normal charging process to attain full capacity of the LMO electrode. Subsequently, the voltage rapidly increased to 4.4 V, at which the BPDB was oxidized, forming the second plateau indicating that the overcharge current is controlled by the "molecular circuit". The cycling was continued until the redox shuttle failed. As shown in Figure 3b, the cell can survive 25 such overcharge cycles before the capacity drops to zero, which we attribute to the eventual consumption of the redox shuttle molecule. The capacity retention profile reveals that the discharge capacity is fading continually during this test, which is possibly due to the ongoing lithium consumption to sustain the solid-electrolyte interphase (SEI) layer on the surface of MCMB.[29]

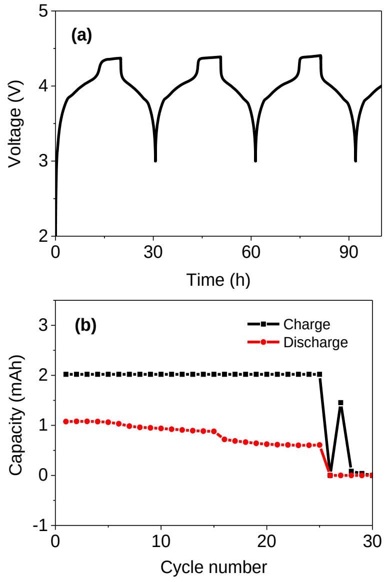

Figure 3. (a) Voltage and (b) capacity retention profiles of overcharge test using MCMB/LMO coin cell containing 5 wt% (0.15 M) BPDB in Gen 2 electrolyte. The charging rate is C/10 and the overcharge ratio is 100%.

While BPDB can clearly serve as a functional redox shuttle additive for the high-voltage cells, the performance is relatively poor. We surmised that a possible reason for the observed deterioration may be due to the decomposition of this molecule on the anode. As we noted above, this reduction is the common concern with the redox shuttles designed for high voltage applications, as it is facilitated by the presence of the same electron withdrawing groups that are introduced to increase the redox potential of the molecule. According to our density functional calculations, the inclusion of the dialkyl phosphine oxide groups makes the gas phase electron affinity of BPDB positive (+ 0.67 eV), whereas for DDB it is negative, i.e. the derivative compound readily accepts an electron. This is confirmed by the chemical reduction of BPDB by potassium metal in dimethoxyethane, which provides similar reducing potential as the cell during formation process. At room temperature, BPDB gradually converted to the radical anion, which was observed using electron paramagnetic resonance spectroscopy, as described in the Supporting Information. The chemically reduced sample was also investigated using proton NMR and the observed new peaks further evidenced the reductive decomposition (Figure S13). The similar coupling patterns of some of the new peaks implied that the decomposition product may have similar functional groups such as isopropyl or benzene ring.

This insight (gained through a chemical means) is also brought out using electrochemical and materials science means. Figure 4a shows the differential capacity profiles that correlate the capacity changes and the cell voltage. In addition to Li intercalation and deintercalation occurring between 3.4 and 4.1 V, there is a peak at 3.0 V which is observed only during the initial charging in cells containing BPDB (see Figure S8), so it originates through a reaction involving this molecule. Evidence for BPDB decomposition in the coin cell is suggested by the changes on the electrode surface morphology. Figure 5 contrasts the scanning electron microscopy (SEM) images of the anodes harvested from cells (i) immediately after the SEI formation and (ii) after the 6th overcharge test cycle. In Figure 5a, where neat Gen 2 electrolyte was used, the anode surface contained well defined MCMB particles, while in the cells containing BPDB, a thick coating was observed after the SEI formation (Figure 5b). This coating became still thicker as the overcharge test continued (Figure 5c), implying the continuous growth of the solid deposit in the presence of BPDB. More SEM images can be found in Figure S10 in the Supporting Information. In contrast, the cathode surfaces did not visibly change independent of the presence of BPDB in the electrolyte (see Figure S11 in the Supporting Information). These results suggest that BPDB continually decomposes on the anode surface. We propose that the reductive decomposition of BPDB (which was also observed in our chemical reduction experiments) not only limits the lifetime of BPDB as a redox shuttle in an electrochemical cell, but also contributes to the consumption of lithium source.

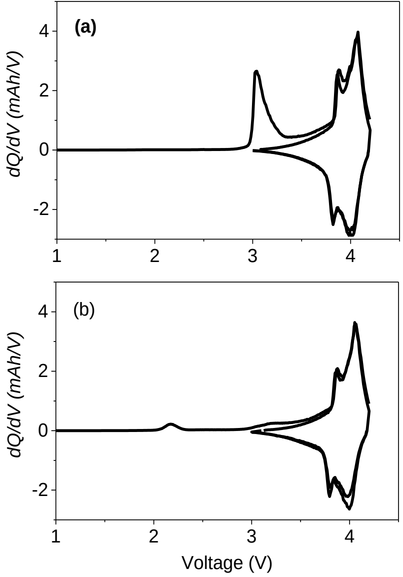

Figure 4. Differential capacity profiles for the formation processes involving LMO and MCMB electrodes in a cell containing 5 wt % BPDB in Gen 2 (a) without LiBOB and (b) with 2 wt% LiBOB.

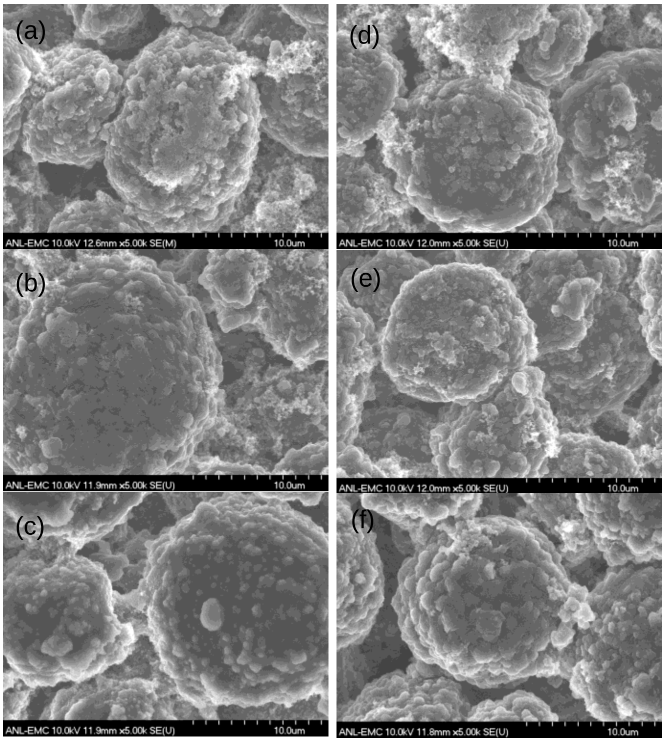

Figure 5. Scanning electron microscopy images of the harvested anodes (a) Gen 2 electrolyte after the 2nd formation cycle; (b) 5 wt% BPDB in Gen 2 electrolyte after the 2nd formation cycle; (c) 5 wt% BPDB in Gen 2 electrolyte after the 6th overcharge cycle; (d) 2 wt% LiBOB in Gen 2 electrolyte after the 2nd formation cycle; (e) 5 wt% BPDB and 2 wt% LiBOB in Gen 2 electrolyte after the 2nd formation cycle; (f) 5 wt% BPDB and 2 wt% LiBOB in Gen 2 electrolyte after the 6th overcharge cycle.

In order to suppress this undesired decomposition of BPDB, lithium bis(oxalato)borate (LiBOB) was used as a supporting electrolyte additive. LiBOB is one of the most effective SEI additives that could protect anode surface by forming a more robust SEI layer.[30-32] When 2 wt% (0.12 M) LiBOB was added (Figure 4b), a new peak at 2.2 V appeared before the BPDB peak during the initial cycle, which corresponds to the reduction of LiBOB (see Figure S9). The 3.0 V feature observed in Figure 4a was greatly reduced, suggesting that BPDB largely remained in the electrolyte. As seen in Figure 5d, with the addition of LiBOB, the anode surface was very similar to that of the Gen 2 electrolyte cell in Figure 5a, and the well-defined MCMB particles were clearly observed. Even with presence of BPDB, the anode surfaces reminded clean both after formation (Figure 5e) and after 6 cycles of overcharge test (Figure 5f). Compared to Figure 5c, the fact of not observing thick coatings on these anode surfaces further confirmed the suppression of BPDB decompositions on the anode surface. As a result, the cell using 5 wt% BPDB and 2 wt% LiBOB survived more than 95 cycles (as shown in Figure 6), indicating the much increased overcharge protection life. While the discharge capacity was still fading, which was possible due to the electrolyte decomposition,[30] this decrease did occur at a slower rate.

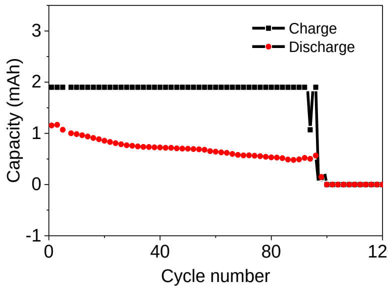

Figure 6. Capacity retention profiles of overcharge abuse test using MCMB/LMO coin cell containing 5 wt% BPDB and 2 wt% LiBOB in Gen 2. The charging rate is C/10 and the overcharge ratio is 100%.

Conclusion

Long-term overcharge protection of LIBs operating above 4 V is a fine balancing act, as the (necessarily) high redox potential of a shuttle molecule generally implies poor electrochemical stability. Our study provides a way of achieving the compromise. Specifically, we demonstrate that BPDB (Figure 1) has a reversible redox potential around 4.5 V *vs.* Li/Li^+ and can provide overcharge protection to MCMB/LMO cells for over 25 cycles with 100% overcharge ratio. While BPDB is stable to oxidation, our experiments suggested that it is much less stable to reduction, as the electron withdrawing groups that are introduced to increase the redox potential also increase the electron affinity of this molecule, making it easier to reduce on the anode. Such concern is inherent in the chemical design of redox shuttle molecules, and so the problem is general. In accord with our spectroscopic studies indicating the occurrence of irreversible decomposition during chemical reduction, careful analysis of differential capacity profiles and electrode surface morphology change indicated that BPDB became reduced on the anode surface causing the inferior performance. By adding a supporting additive, this undesired decomposition was suppressed and the overcharge protection was increased from 25 cycles to more than 95 cycles. Our study thus proves that the optimum can indeed be found, and it encourages further search of still better performing overcharge protection additives.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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