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REDOX SHUTTLE ADDITIVES FOR OVERCHARGE PROTECTION IN LITHIUM BATTERIES

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ABSTRACT

Seven new redox shuttle additives with shuttle current onset potentials above 4.2 V vs Li/Li^+ are reported, along with diffusion coefficients for the neutral additives. The dependence of the limiting shuttle current on the respective diffusion coefficients of the oxidized and reduced forms of an additive is clarified. Overcharge protection in liquid electrolyte $Li/LiMn_2O_4$ cells is demonstrated.

INTRODUCTION

Reliable and inexpensive overcharge protection for multi-cell lithium battery stacks is a major obstacle to commercialization of these promising systems in electric vehicles and other high voltage applications. Severe overcharging can not only reduce rechargeable capacity and cell life, but can also create hazardous conditions. Even moderate overcharging of transition metal oxide cathodes often leads to structural and compositional changes in the oxide matrix which have significant effects on their subsequent cycling behavior (1).

The redox shuttle approach to overcharge protection employs an electrolyte additive which acts as an internal current shunt when the positive electrode potential exceeds the oxidation potential of the additive (2-4). The ability of organic aromatic compound additives to extend cell life in transition metal oxide lithium solid polymer electrolyte cells under conditions of moderate to severe overcharging has previously been demonstrated (5). Recently, several new additives have been reported for both polymer electrolyte (6) and 4 V lithium ion cells (7).

The redox shuttle effect may be observed in any electrochemical system in which a soluble redox couple is present. When utilized for overcharge protection, the additive is present in the electrolyte in its reduced form during normal cell operation (discharging, storage, charging to capacity), and has little or no effect on cell performance. On overcharging, i.e. when the positive electrode potential exceeds the additive's onset potential, it is electron oxidized to a soluble species which diffuses toward the negative electrode, where it is reduced to its original state. This allows current to flow through the cell without damage due to overcharging.

It can be shown that for a one-electron couple with efficient charge transfer kinetics, the limiting shuttle current density in a flat plate cell with all of the electrolyte between the electrodes is given by:

$$i_{\lim} = \frac{FC_o}{\frac{L}{2}\left(\frac{1}{D_R} + \frac{1}{D_O} \right)} \qquad [1]$$

where C_o is the initial concentration of the additive, L is the separator thickness, and D_r and D_o are the diffusion coefficients of the reduced and oxidized forms of the additive. It is clear from Eq. 1 that the maximum shuttle current is limited by the diffusion rate of the slower moving species. The additive may be molecular or ionic. In general, charged species have smaller diffusion coefficients than neutral molecules, so that for the molecular additives studied in this work, the shuttle current is limited by diffusion of the radical cations or dications formed at the positive electrode.

It can also be shown that the average concentrations of the reduced and oxidized forms of the additive when the limiting current is reached are inversely proportional to their respective diffusion coefficients (Eq. 2). Thus, a shuttle additive whose oxidized form

$$\overline{C}_R = \frac{L}{2}\frac{i_{\lim}}{FD_R}, \qquad \overline{C}_O = \frac{L}{2}\frac{i_{\lim}}{FD_O} \qquad [2]$$

diffuses an order of magnitude slower than its reduced form will be about 90 % converted to the oxidized form when carrying the maximum shuttle current.

EXPERIMENTAL

The redox properties of a number of molecular additives were studied using a platinum microelectrode with a diameter of 10 μm in a flooded cell with lithium foil counter and reference electrodes. Cyclic voltammogrammes were recorded using an EG&G PAR 273A potentiostat. Electrolytes contained an additive at 0.1 M concentration and 1M $LiPF_6$ in a 1:1 mixture of ethylene carbonate and propylene carbonate (EC:PC) or a 1:2 mixture of ethylene carbonate and dimethyl carbonate (EC:2DMC). The microelectrode potential was swept between 3.0 V and 5.0 V at a rate of 20 mV/s. All preparations and tests were carried out in an inert atmosphere glovebox with oxygen content < 1 ppm and water < 5 ppm. $LiMn_2O_4$/Li cells were assembled using polypropylene compression fittings with stainless steel current collectors and Celgard

3401 separators (50µm). Galvanostatic cycling was performed using an Arbin battery testing system.

RESULTS AND DISCUSSION

Microelectrode cyclic voltammogrammes showing onset potentials and limiting currents for seven new additives and two of the additives reported by SONY (Ref. 7) in EC:2DMC are shown in Figure 1. Additive SONY 1 is 4-fluoro-1,2-dimethoxybenzene and SONY 2 is 4-bromo-1,2-dimethoxybenzene.

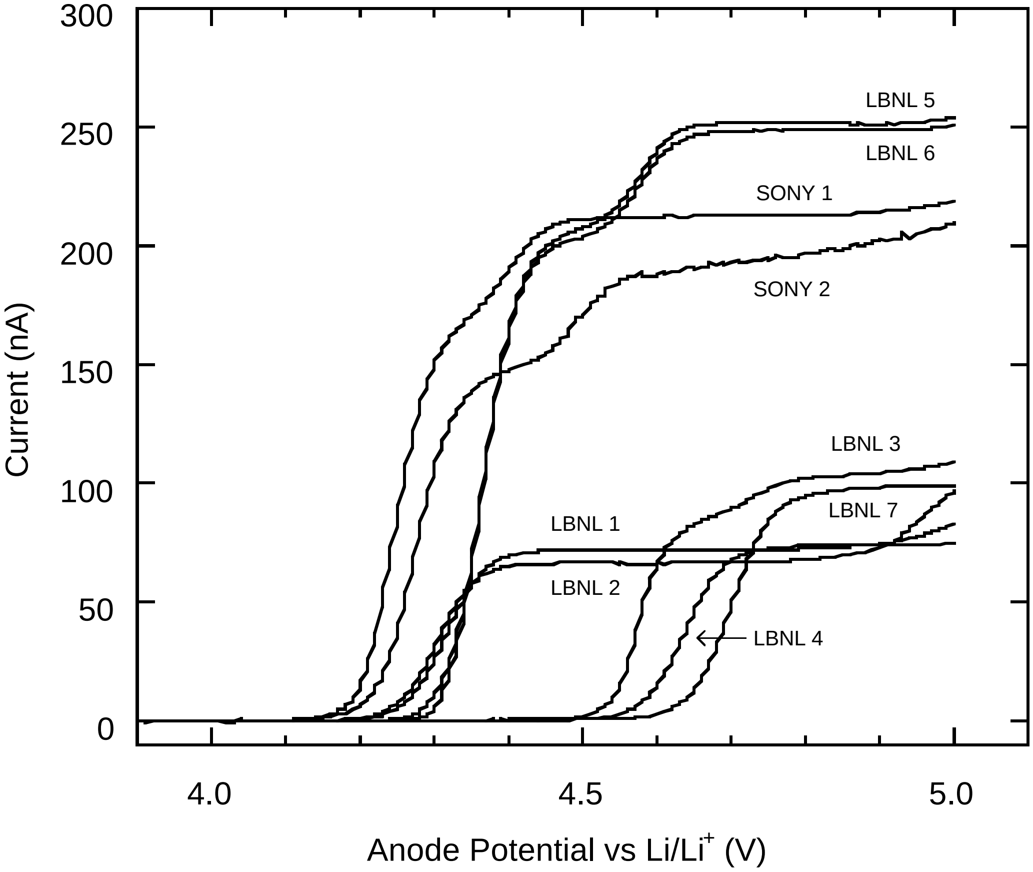

Figure 1. Microelectrode cyclic votammogrammes for redox shuttle additives in 1.0 M $LiPF_6$ EC:2DMC.

Diffusion coefficients for the neutral molecules can be calculated from the observed limiting currents at the microelectrode according to Eq. 3, in which *r* is the radius of the microelectrode.

$$D_R = \frac{i_{\lim}}{4nrFC_b} \qquad [3]$$

Shuttle current onset potentials and molecular diffusion coefficients for these additives are given in Table I. Some additives exhibit a two-step oxidation process, with the second step about 30 mV above the first. This is probably due to formation of a singly charged complex between the radical cation produced in the first step (Eq. 4) and a neutral additive molecule (Eq. 5). The dimeric monocation is subsequently oxidized and dissociated to two radical cations at a slightly higher potential (Eq. 6). This mechanism may reduce

$$A \rightarrow A^+ + e^- \qquad [4]$$

$$A^+ + A \rightarrow A_2^+ \qquad [5]$$

$$A_2^+ \rightarrow 2A^+ + e^- \qquad [6]$$

somewhat the calculated value of D_r for these additives, due to consumption of neutral molecules by dimer formation.

Table I. Onset potentials and reduced-form diffusion coefficients.

Additive	Onset Potential (V)	D_r (10^{-6} cm^2/s)
SONY 1	4.15	8.9
SONY 2	4.15	7.6
LBNL 1	4.20	3.7
LBNL 2	4.20	3.4
LBNL 3	4.50	4.4
LBNL 4	4.54	3.8
LBNL 5	4.25	10.9
LBNL 6	4.27	10.5
LBNL 7	4.60	5.1

The dramatic effect of solvent viscosity on observed diffusion rates is illustrated in Fig. 2. The microelectrode limiting current is three times as high in the lower viscosity EC:2DMC mixture than in EC:PC.

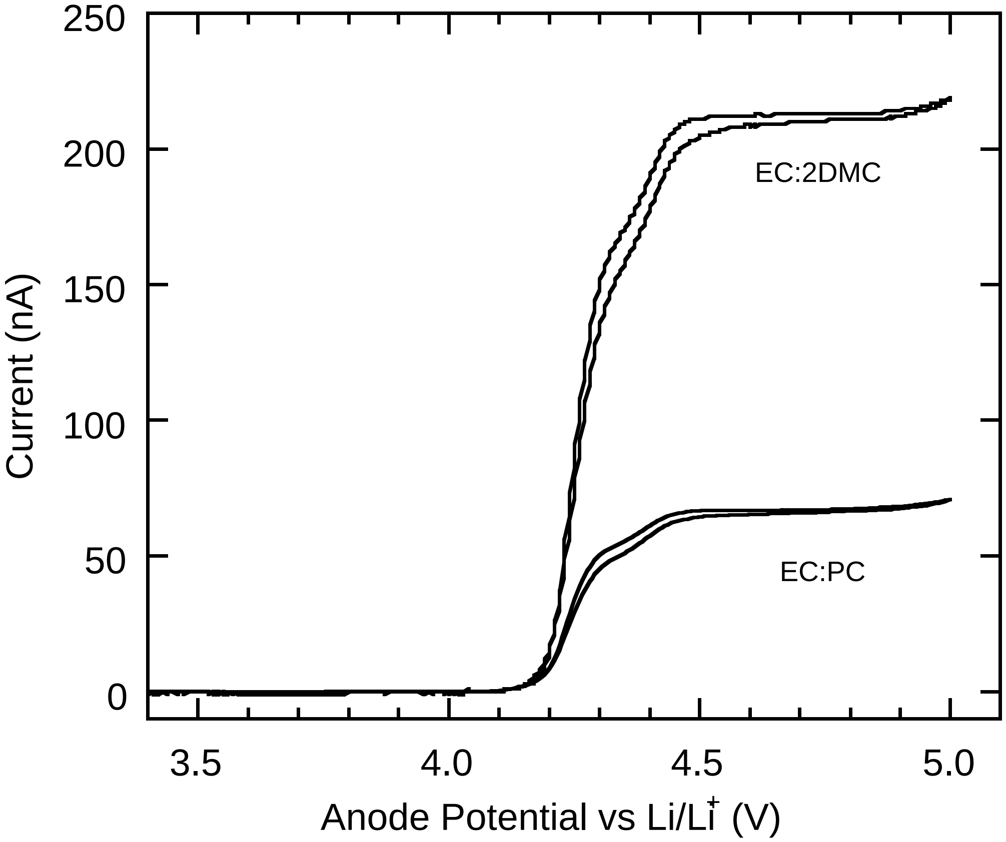

Figure 2. Microelectrode cyclic votammogrammes for additive SONY 1 in EC:2DMC vs. EC:PC (1.0 M $LiPF_6$).

The ability of a redox additive to protect a $LiMn_2O_4$/Li cell from capacity loss due to overcharging was examined. The electrolyte was a 0.5 M solution of additive LBNL 1 in 1.0 M $LiPF_6$ in EC:2DMC. Charging and discharging at 0.25 mA/cm^2 (C/7 rate) with an upper limit of 4.2 V and a lower limit of 3.5 V produced a constant discharge capacity of 100 mAh/g over five cycles, with a coulombic efficiency of 97 %. The voltage profile for the fifth cycle is the lower trace in Figure 3. Profiles for the first four cycles were nearly identical with the fifth, and were omitted for clarity. Beginning with the sixth cycle, charging was continued for an additional 3 h, a 43 % increase in charge capacity. The voltage profiles for cycles 6 through 10 (Fig. 3) show a small initial increase in discharge capacity, followed by a gradual decline. The coulombic efficiencies for these cycles are between 63 and 73 %, reflecting substantial overcharging of the cell.

A significant depression in the discharge voltage profiles was observed following overcharging. The voltage plateaus characteristic of the spinel electrode were still present, however, the depression was the same for each subsequent cycle, and the cell potential rapidly returned to its expected level when the discharge was interrupted. The voltage drop is therefore due to an increase in internal resistance, rather than electrode damage or accumulation of a deposit on either electrode. The origin of this resistance is most likely the depletion of lithium ions in the electrolyte during oxidation of the redox additive. As the additive is oxidized at the positive electrode (Eqs. 4-6), lithium ions are reduced at the negative electrode. During normal charging of the cell, these lithium ions are replaced by extraction from the positive electrode, maintaining a constant overall Li^+ concentration in the electrolyte.

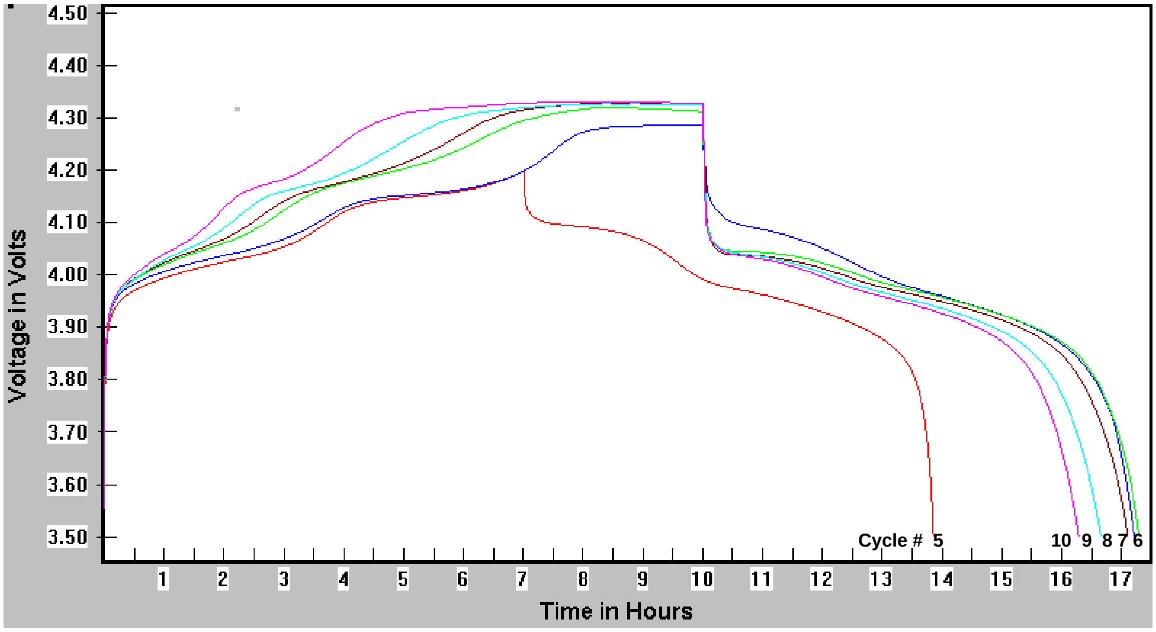

Figure 3. Galvanostatic cycling of additive-protected $LiMn_2O_4$/Li cell.

Inefficient charge transfer at the negative electrode hinders reduction of the oxidized shuttle additive and contributes to depletion of lithium ions. This is because (unlike lithium ions) the relatively large radical cations do not readily penetrate the solid electrolyte interface (SEI) layer on the lithium foil surface. This severely restricts the shuttle current to a much lower level than would be expected for a cell of these dimensions. Use of a carbon anode, with a much larger surface area and smaller SEI thickness than that on Li foil, is expected to mitigate this problem. Preliminary experiments with Li-ion cells have been encouraging.

The solubility of the oxidized form of the additive is also a crucial issue. Precipitation of radical cation salts of certain additives from $LiPF_6$ solutions has been observed. Proper selection of solvents and the use of mixed salt electrolytes may help to mitigate this problem.

CONCLUSIONS

Redox shuttle additives with shuttle current onset potentials well above those required for full charging of positive electrodes used in lithium and lithium ion batteries are now available. The maximum current carried by the additive depends upon the separator thickness, electrolyte composition, and additive concentration. The ability of such additives to maintain discharge capacity despite significant overcharging has been demonstrated in $LiMn_2O_4$/Li cells. Improved protection and higher shuttle currents are expected in lithium ion cells. Further investigation is needed to determine whether redox shuttle additives can also improve the safety of lithium batteries.

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