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Short communication

Application of a nitroxide radical as overcharge protection in rechargeable lithium batteries

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Abstract

Redox shuttle electrolyte additives have been suggested as a possible mean of internal overcharge protection of secondary lithium-ion batteries. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is one of these redox shuttles for overcharge protection of 3 V class Li-ion cells. The electrochemical reversibility and the diffusion coefficient of this molecule has been evaluated by mean of cyclic voltammetry. The redox shuttle voltage was found to be 3.5 V versus Li/Li$^+$ and $D = \text{cm}^2\ \text{s}^{-1}$. The electrochemical stability of TEMPO in different overcharging conditions has been evaluated by long-term cycling using Li/Li$_4$Ti$_5$O$_{12}$ cells. Results show that the TEMPO redox system does not act as an ideal shuttle. When dissolved in the electrolyte at 0.5 M, this additive is able to level off the cell potential at 3.5 V for a long period at low overcharging current (C/200 to C/50). Nevertheless, it appears that the cell capacity fades drastically at the first cycles and with time. This phenomenon is probably related to the stability of the oxidized and reduced form of the TEMPO molecule.

Keywords: Secondary lithium-ion batteries; Overcharge protection; TEMPO; Redox shuttle; Electrochemical stability

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1. Introduction

One problem encountered in the development of rechargeable lithium batteries is the protection of individual cells from overcharging. When lithium-ion cells are assembled in batteries, it is necessary to protect each of them from overcharging by an electronic device (active by-pass). This increases the complexity and the cost of the batteries, especially for space applications where the requirements for reliability is high. When the applied tension exceeds the maximum voltage of the cell, the oxidation of the electrolyte occurs. The oxidation of the electrolyte is accompanied in general by gas evolution (mainly CO$_2$ in presence of alkylcarbonate solvents) which causes an increase in the internal pressure of the cell [1–5].

This process causes a consumption of electrolyte which reduces the capacity and the calendar life of the accumulator. There have been several reports [6–9] on chemical prevention of the overcharge of lithium rechargeable batteries. These reports concern 3 V and 4 V class batteries in which redox reagents such as derivatives of ferrocene and aromatic compounds are used. Recently, Dahn [10–13] demonstrates the effectiveness of 2,5-diterbutyl-1,4-dimethoxybenzene as a redox shuttle additive of LiFePO$_4$ based Li-ion cells, this molecule has a defined redox potential at which it is oxidized at the positive electrode. The oxidized shuttle diffuses then to the negative electrode and the reverse reaction occurs. This process continues until charging is terminated. The net effect is an internal shunt which prevents damage to the cell by imposing a limit in cell potential.

We wish to report our results for the study of TEMPO as chemical shuttle additives for rechargeable Li/Li$_4$Ti$_5$O$_{12}$ cells.

2. Experimental

TEMPO (purity >99.99%) and derivatives (acetamido-TEMPO and cyano-TEMPO (purity >99.99%)) are obtained from Aldrich and used as received. LiPF$_6$ (99.99%) was purchased from Aldrich. The EC/DEC (2/3, v/v) + LiPF$_6$ (1 M) reference electrolyte was prepared by volume in a dry box. The water content of the solvents was less than 20 ppm as indicated by Karl Fischer titration. TEMPO was dissolved into the electrolyte at the concentration of 0.0125 M and 0.5 M.

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Table 1
Charge–discharge and overcharge program used in cycling experiments

Step 1: discharge	Step 2: charge	Step 3: overcharge
Rate: $C/5$ Cut off: $E = 1.1$ V	Rate: $C/5$ Cut off: $E = 3$ V	Rate: $C/50$ Charge timed after 2.5 h
Rate: $C/5$ Cut off: $E = 1.1$ V	Rate: $C/5$ Cut off: $E = 3$ V	Rate: $C/200$ Charge timed after 10 h

Cyclic voltammetry was performed using a three-electrode cell connected to a radiometer potentiostat (Voltalab PGZ10). A glassy carbon disk (3 mm in diameter) was used as working electrode and metallic lithium as reference and counter electrodes. All potentials are shown in reference to the Li/Li$^+$ system. Voltage scanning was run in the range 3.2–4 V at a different scan rates (5 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1}, 100 mV s^{-1}, 150 mV s^{-1} and 200 mV s^{-1}).

Charge–discharge tests were performed by dissolving the shuttle molecule in the electrolyte contained in Li/$Li_4Ti_5O_{12}$ half cells. The lithiated titanate electrode ($Li_4Ti_5O_{12}$) is a gift from SAFT. Li/$Li_4Ti_5O_{12}$ half cells were built using Swagelok connectors and cycled with an Arbin battery cycler. Two kinds of separator were used, a CELGARD®.

Two thousand three hundred and twenty membranes and a polypropylene felt (Villedon®). Half cells were discharged at $C/5$ rate to a low cut off voltage of 1.1 V. Charge was operated at the same constant current from 1.1 V to 3 V. At potentials higher then 3 V overcharge occurs and the charge–discharge rate was reduced. Overcharge test were run using different conditions is summarized in Table 1.

3. Results and discussion

Key criterions for the selection of a good chemical shuttle are:

(i) The reversibility of the redox reaction. This is indeed the first prerequisite to obtain the above defined electrochemical shuttle effect.
(ii) The redox potential of the shuttle additive. This redox potential should be about 300 mV above the normal maximum operating potential of the positive electrode, in order to avoid self-discharge of the cell by the shuttle.
(iii) The diffusion coefficient of the shuttle must be large in order to carry the overcharge current imposed to the cell.

3.1. Reversibility and redox potential of TEMPO and TEMPO derivatives

The electrochemical reversibility of the TEMPO molecule was studied by cyclic voltammetry. Typical voltamograms are displayed in Fig. 1. During the positive sweep, TEMPO is oxidized into the corresponding oxoammonium TEMPO$^+$ cation. During the negative sweep TEMPO$^+$ is reduced back into its neutral redox form. The TEMPO/TEMPO$^+$ redox system appears as reversible at scan rates below 100 mV s^{-1} as the difference between the anodic and cathodic half peak potentials is equal to 60 mV. The standard potential of this system evaluated by $(E_{p1/2,a} + E_{p1/2,c})/2$, is 3.5 V. Moreover the peak areas under the anodic and cathodic sweep are equal even at the maximum scan rate of 200 mV s^{-1}.

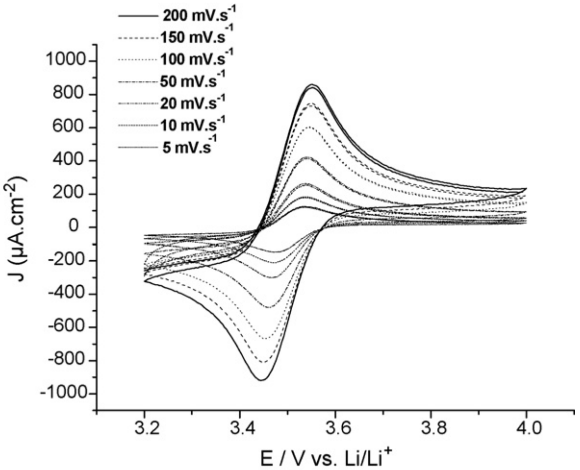

Fig. 1. Cyclic voltamograms of 0.0125 M TEMPO in EC/DEC + $LiPF_6$ 1 M at different scan rates.

TEMPO derivatives such as cyano-TEMPO and acetamido-TEMPO were studied in order to determine the influence of constituent groups on the shuttle redox potential. In Table 2 are reported the redox potentials of these molecules. The introduction of a cyano or acetamido group increases the redox potential of the TEMPO molecule as predicted by Hammett substitutes values for an electro-attractive group. In accordance with previous results [14], the redox potential of acetamido-TEMPO is shifted by +300 mV relative to TEMPO. The redox potential of cyano-TEMPO is shifted only by +150 mV. Nevertheless, the redox potential of these TEMPO derivatives remain to low for use with a $LiCoO_2$ electrode and it will be difficult to synthesis TEMPO derivatives having a standard potential 0.8 V more positive than the parent molecule.

3.2. Diffusion coefficient and by-pass current

The TEMPO diffusion coefficient has been determined by plotting the anodic peak current density versus the square root of the sweep rate (Fig. 2) and using the Randles–Sevcik equation:

$$J_p = 2.69 \times 10^5 n^{3/2} D^{1/2} v^{1/2} C \qquad (1)$$

In Eq. (1) J_p is the anodic peak current density, n the number of electrons involved in the redox reaction (one in our case), v the voltage sweep rate, C the shuttle concentration (12.5 mol cm^{-3}) and D is the diffusion coefficient. The diffusion coefficient was

Table 2
Redox potentials of TEMPO, cyano-TEMPO and acetamido-TEMPO determined by cyclic voltammetry

Molecule	TEMPO	Cyano-TEMPO	Acetamido-TEMPO
E_{eq} vs. Li/Li$^+$	3.60	3.74	3.90
ΔE (mV)	0	140	300

ΔE is the difference between the redox potential of the TEMPO and its derivative.

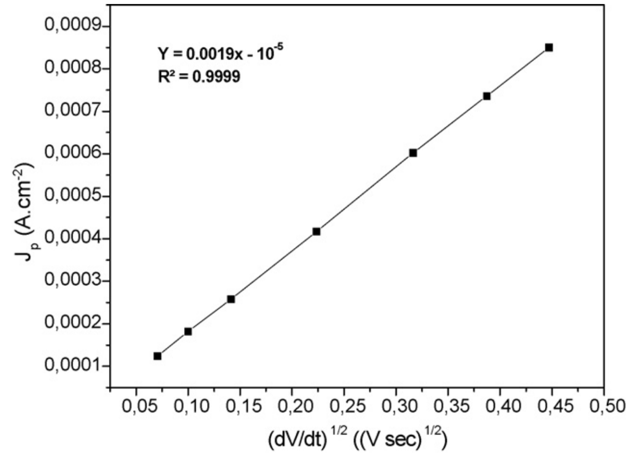

Fig. 2. Evolution of J_p vs. the square root of the sweep rate for a 0.0125 M TEMPO solution in the electrolyte.

deduced from the slope of the graph reported in Fig. 2, taking into account the working electrode surface area (0.07 cm^2), $D = 2.37.10^{-5}$ $cm^2\ s^{-1}$.

In order to determine the by-pass current, i.e. the maximum current that a shuttle can carry, chronoamperometry experiments were carried out at different imposed potential. In Fig. 3 is displayed the chronoamperometric response for electrolyte solutions containing TEMPO at the concentration of 0.1 M. The by-pass current increases with the applied tension until a maximum which is reached for $E = 3.8$ V. Beyond this value, the current carried by the shuttle is levelled at 0.95 mA. Hence, the maximum current density that can be carried by the shuttle at the concentration of 0.1 M, is 14 mA cm^{-2}.

3.3. Electrochemical stability of TEMPO in long-term cycling at low overcharge rates in Li/$Li_4Ti_5O_{12}$ cells

The electrochemical stability of TEMPO in long-term cycling at low overcharge rates has been explored using Li/$Li_4Ti_5O_{12}$ cells. C/10, C/50 and C/200 overcharge rates were tested which correspond, respectively, to overcharging current (expressed in mA g^{-1} of active material) of 38.62 mA g^{-1}, 7.72 mA g^{-1} and 1.93 mA g^{-1}. Fig. 4a shows the cell potential plotted versus time for a Li/$Li_4Ti_5O_{12}$ cell containing 0.5 M of TEMPO and using a C/10 charging rate. The graph displayed in this figure shows that the voltage increases instead of leveling off at $E = 3.5$ V versus Li/Li^+ as expected.

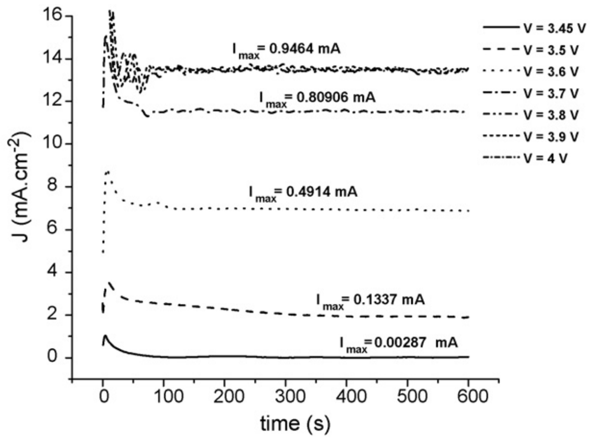

Fig. 3. Chronoamperogram at various potential from 3.45 V to 4 V of the cell containing 0.1 M TEMPO in EC/DEC + $LiPF_6$ 1 M.

The limiting diffusion current that can be carried by a shuttle molecule between two planar electrodes is given by the following equation:

$$J_{\max} = \frac{nFDC}{L} \qquad (2)$$

In this equation, n is the number of elementary charges carried by the shuttle (one in our case), F the Faraday's number, A the area of the planar electrodes, D the diffusion coefficient of the shuttle, C the shuttle concentration (0.5 M) and L is the electrode spacing (150 μm). Using the numerical values of all the parameters reported in Eq. (2), one obtains $J_{\max} = 76$ mA cm^{-2}. As the applied current density ($J = 0.28$ mA cm^{-2}) imposed to the cell at the C/10 charge rate is much lower that the theoretical maximum current density ($J \ll J_{\max}$), it is inferred that the separator (Celgard®) limits the current density. Another possible reason for the observed low limiting current density could be related to the stability of the oxoammonium cation or/and

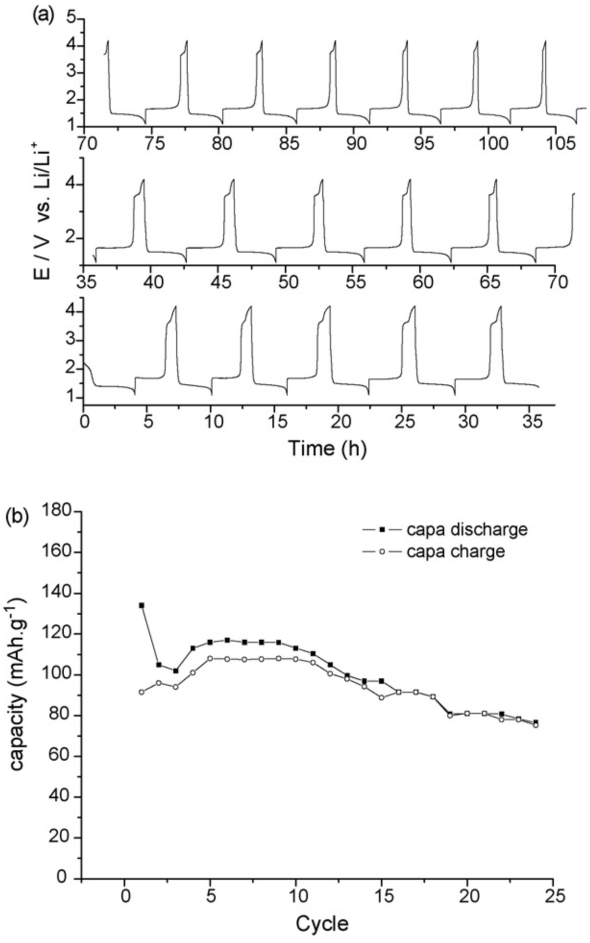

Fig. 4. (a) Potential vs. time evolution for Li/$Li_4Ti_5O_{12}$ cell containing 0.5 M TEMPO and cycled at C/10 overcharge rate. (b) Positive electrode specific capacity vs. cycle number for the same cells.

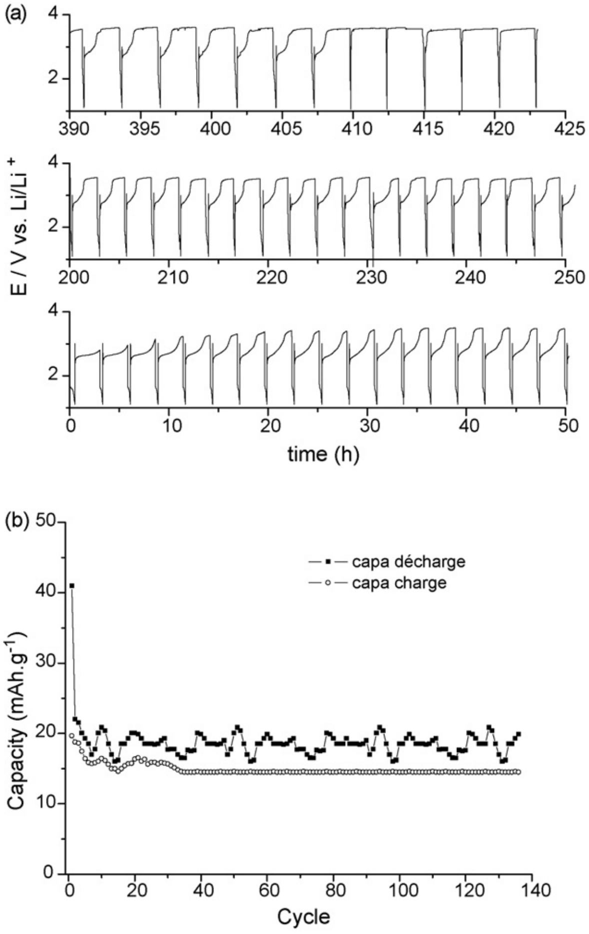

Fig. 5. (a) Potential vs. time evolution for a Li/$Li_4Ti_5O_{12}$ cell containing 0.5 M TEMPO, and cycled at *C*/50 overcharge current. (b) Positive electrode specific capacity vs. cycle number for the same cell.

to the stability of the TEMPO itself in the presence of metallic lithium.

Fig. 4b shows the charge and discharge capacity of the Li/$Li_4Ti_5O_{12}$ cell versus cycle number. It is noticed that the presence of TEMPO modifies the cyclability of the positive electrode. A sharp capacity loss is observed since the first cycle, as the electrode capacity in the reference electrolyte is 150 mAh cm^{-2} [15,16]. Moreover, after only 25 cycles, the specific capacity drops to 80 mAh g^{-1} which means that the shuttle molecule has a detrimental effect on the cycling properties of the electrode.

In Fig. 5a is plotted the potential against time for Li/$Li_4Ti_5O_{12}$ cell containing 0.5 M of TEMPO. Fig. 5b shows the positive electrode specific capacity, deduced from the proceeding graph, as a function of the cycle number. The charge–discharge program for this test is reported in Table 1. The plot in Fig. 5a shows that the shuttle carries the overcharging current ($I = 0.056$ mA) for over 100 cycles at $E = 3.5$ V, which is exactly the redox potential of the TEMPO redox system. Fig. 5b demonstrated that the presence of the shuttle molecule in solution impedes almost completely insertion or extraction of lithium-ions from the electrode active material as the capacity is very low (less than 20 mAh g^{-1}).

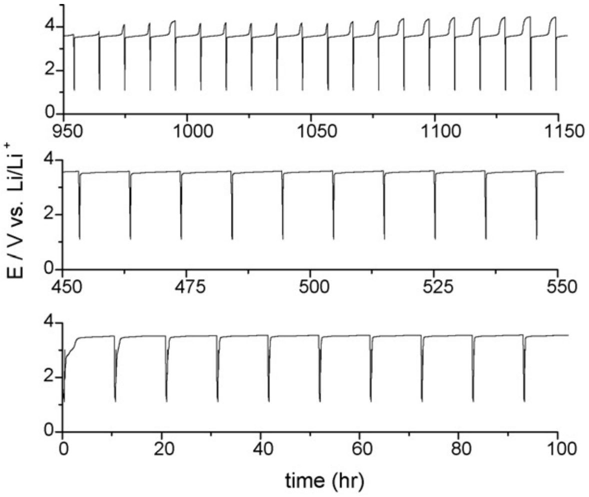

Fig. 6. Evolution of potential vs. time for Li/$Li_4Ti_5O_{12}$ cell containing 0.5 M TEMPO as the shuttle molecule overcharged at *C*/200 rate.

Fig. 6 shows the Li/$Li_4Ti_5O_{12}$ cell potential, plotted versus time, in the presence of 0.5 M of TEMPO at *C*/200 overcharge rate. Results confirm those obtained from the graphs reported in Fig. 5a. A plateau near 3.5 V is observed which correspond to the oxidation of the TEMPO molecule at the $Li_4Ti_5O_{12}$ electrode and its corresponding reduction at the lithium electrode. Even at this very low overcharging rate, the presence of TEMPO in the formulation of the electrolyte prevents almost completely the cyclability of the positive electrode. We speculate that the reason for this is related to the stability of the TEMPO oxidized and reduced forms resulting in the formation of a passivating layer on the positive electrode.

4. Conclusion

The redox reaction of the TEMPO/$TEMPO^+$ system is focused around 3.5 V. Even if the electrochemical reversibility of this system is high, it did not work well as an additive for overcharge protection. At moderate overcharge rates (*C*/10) and in the cell configuration used in this study, the TEMPO molecule is not able to level off the cell voltage at its potential of oxidation. At lower overcharge rates, such as *C*/50, *C*/100 or *C*/200, the voltage of the cell is effectively levelled off at 3.5 V. Nevertheless the charge–discharge cell capacity becomes very low as compared to what is obtained in the absence of this additive.

Why TEMPO does not act as a perfect shuttle molecule? A possible cause is the low stability of the $TEMPO^+$ cation or/and TEMPO itself toward the electrodes which results in the formation of a passive layer on the positive electrode. This layer will impede, at least partially, the Li^+ ions insertion–deinsertion mechanism in the positive electrode. The identification of the nature of this layer and the study of its formation will be the goal of future work.

References

[1] F. Blanchard, B. Carré, F. Bonhomme, P. Biensan, D. Lemordant, Can. J. Chem. 81 (2003) 385–391.

[2] E. Cattaneo, B. Rasch, W. Vielstich, J. Appl. Electrochem. 21 (1991) 885.
[3] G. Eggert, J. Heitbaum, Electrochim. Acta 81 (1986) 1443.
[4] R. Imhof, P. Novak, J. Electrochem. Soc. 146 (1999) 1702.
[5] B. Rasch, E. Cattaneo, P. Novak, W. Vielstich, Electrochim. Acta 36 (1991) 1397.
[6] S.R. Narayanan, S. Surampudi, A.I. Attia, C.P. Bankston, J. Electrochem. Soc. 138 (1991) 8.
[7] K.M. Abraham, D.M. Pasquariello, E.B. Willstaedt, J. Electrochem. Soc. 137 (1990) 1856.
[8] M. Neal Golvin, D.P. Wilkinson, J.T. Dudley, D. Holonko, S. Woo, J. Electrochem. Soc. 139 (1992) 8.
[9] M. Adachi, K. Tanaka, K. Sekai, J. Electrochem. Soc. 146 (1999) 1256.
[10] C. Buhrmester, J. Chen, L. Moshurchak, J. Jiang, R. Liangchen Wang, J.R. Dahn, J. Electrochem. Soc. 152 (2005) A2390–A2399.
[11] J. Chen, C. Buhrmester, J.R. Dahn, Electrochem. Solid-State Lett. 8 (1) (2005) A59–A62.
[12] L.M. Moshurchak, C. Buhrmester, J.R. Dahn, J. Electrochem. Soc. 152 (2005) A1279.
[13] J.R. Dahn, J. Jiang, M.D. Fleischauer, C. Buhrmester, L.J. Krause, J. Electrochem. Soc. 152 (2005) A1283.
[14] T. Breton, D. Liaigre, E.M. Belgsir, Tetrahedron Lett. 46 (2005) 2487–2490.
[15] C.H. Chen, J.T. Vaughey, A.N. Jansen, D.W. Dees, A.J. Kahaian, T. Goacher, M.M. Thackeray, J. Electrochem. Soc. 148 (2001) A102.
[16] T. Ohzuku, A. Ueda, N. Yamamoto, J. Electrochem. Soc. 142 (1995).