

In situ UV–visible spectroscopy: characterization of overcharge protection additives for secondary lithium batteries

T.J. Richardson^{*}, P.N. Ross Jr.

Chemical Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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Abstract

A technique has been developed for in situ measurement of UV–visible spectra of lithium battery electrolytes. The method has been applied to the investigation of the redox properties and diffusion characteristics of electrolyte additives for overcharge protection in secondary lithium batteries. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Battery life; Lithium batteries; Organic electrolytes; Spectroscopy; Redox processes

1. Introduction

Electrochemical storage batteries of all types are susceptible to damage due to overcharging. The effects may include degradation of electrodes, current collectors, electrolytes and separators. Internal shorting and/or gas evolution can result in cell failure and/or dangerous runaway reactions. While protection of a single cell or a small stack of series-connected cells may be achieved through direct monitoring and control of charging rates and state of charge of individual cells. This may be impractical for large stacks of the size required for use in electric vehicles. The redox shuttle approach to overcharge protection employs an electrolyte additive which acts as an internal current shunt when the charging potential exceeds the oxidation potential of the additive. Applications of this concept to overcharge protection in rechargeable lithium batteries utilizing liquid electrolytes have been reported [1–10]. The ability of such additives to extend cell life in transition metal oxide lithium solid polymer electrolyte cells under conditions of moderate to severe overcharging has recently been demonstrated [11]. Although important performance parameters including shuttle onset potential, current limitations, and ‘effective’ diffusion coefficients can be determined from potential sweep measurements, the identity of the diffusing species and their individual contributions to the shuttle current remain unknown.

The redox additives considered here are aromatic neutral molecules or anions. The oxidized or reduced form of the shuttle (or both) may have absorption bands in the visible and/or near UV spectrum. When the additive is oxidized or reduced at the working electrode, lithium ions must be taken up or released by the counter electrode. Spectroelectrochemical measurements are commonly made in a liquid cell with a large electrolyte reservoir and a counter electrode which is out of the light path. In lithium batteries, however, the electrolyte is contained in the thin separator between parallel electrodes. In order to closely approximate these conditions, the spectroelectrochemical cell must utilize a counter electrode comprised of a lithium ion intercalation compound which remains nearly transparent throughout the experiment. The material used here is lithium vanadium oxide, $\text{Li}_x\text{V}_2\text{O}_5$. Similar cells have been used to study electrochromic intercalation electrodes and electropolymerization on electrode surfaces. We believe this is the first application to solution redox electrochemistry. The redox additives considered here are aromatic neutral molecules or anions. The oxidized or reduced form of the shuttle (or both) may have absorption bands in the visible and/or near UV spectrum. We have developed a technique, using a transparent lithium ion intercalation electrode, which allows us to measure the spectrum of one or more of the redox-active species as a function of potential, current, charge, or time in liquid, polymer, and gel electrolyte cells. Because all of the electrolyte is contained between the electrodes, lateral diffusion is absent, as is convection in polymer and gel electrolytes. The

^{*} Corresponding author. Tel.: +1-510-486-8619; Fax: +1-510-486-6033; E-mail: tjrichardson@161.gov

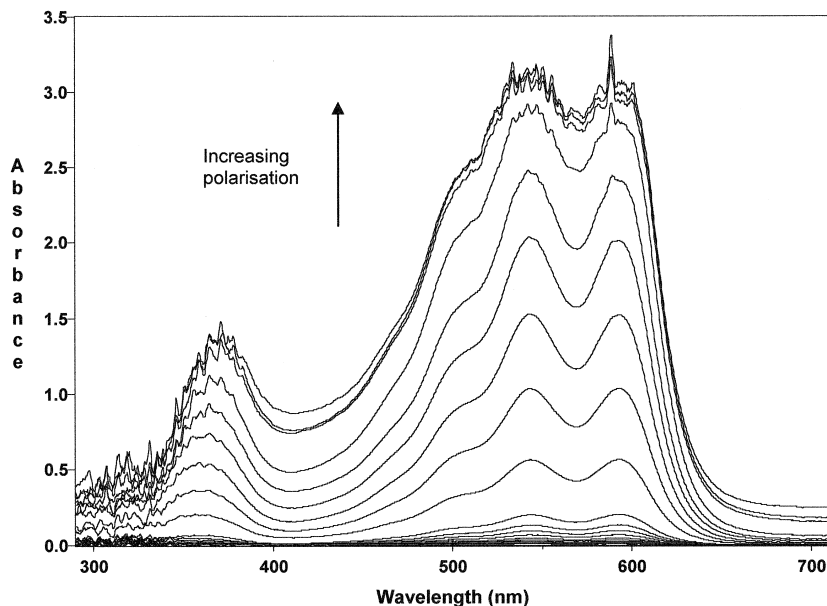


Fig. 1. Visible spectrum of TMPD^+ at varying applied potentials of 0 V to 2.0 V in 0.1 V steps.

absorbance spectrum can therefore provide a direct measure of the concentration of electroactive species. When this is monitored as a function of time following an applied potential step, the diffusion coefficient of the reacting species can be determined even in the presence of parasitic currents or slow charge transfer.

2. Experimental

Glass plates coated with a thin layer of fluorine-doped tin oxide ($\text{SnO}_2:\text{F}$) having a sheet resistance of $15 \Omega/\square$ (Donnelly) were used as transparent active working electrodes and as current collectors for transparent $\text{Li}_x\text{V}_2\text{O}_5$ thin film counter electrodes. The latter (ca. 100 nm thick) were prepared by spin-coating $\text{SnO}_2:\text{F}$ -coated plates with a solution of vanadium triisopropoxide in ethanol, and heating them in air for 1 h at 500°C . The resulting yellow films become a very pale violet in color following initial electrochemical lithium insertion and have thereafter a non-electrochromic reversible capacity for Li intercalation of about $5 \mu\text{A h cm}^{-2}$. Two-electrode spectroscopic cells were prepared using polymer, gel, and liquid non-aqueous lithium electrolytes. Those detailed herein utilized a gel composed of 1 M LiClO_4 in propylene carbonate (PC) immobilized in a polyvinylidene difluoride (PVDF) membrane (Gelman FP Vericel). The separator was transparent, had a uniform thickness of $150 \mu\text{m}$ and contained about 85% electrolyte by weight. The cells were assembled in an inert atmosphere box and sealed at the edges with low vapor-pressure epoxy (Torr-seal, Varian). Spectra were obtained over the range 160 to 880 nm using a fiber optic CCD grating spectrometer (Ocean Optics). The active electrode areas were 5 cm^2 , and the illuminated area was 5

mm^2 . Except under very strong polarization, the steady-state coloration was uniform throughout the cell. The use of a metallic lithium reference electrode is impracticable due to its reactivity toward the oxidized form of the additive. Attempts to incorporate a pseudoreference electrode from an isolated portion of the counter electrode were unsuccessful due to diffusion of electroactive species throughout the cell.

3. Results and discussion

Redox shuttle currents are carried by additive molecules or ions that are oxidized at the positive electrode, diffuse through the electrolyte, and are reduced at the negative electrode. When in situ UV-vis a cells containing redox active electrolyte additives are polarized, spectral changes

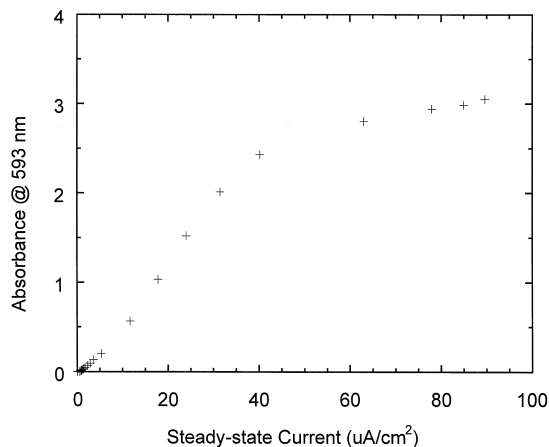


Fig. 2. TMPD^+ absorbance vs. current density.

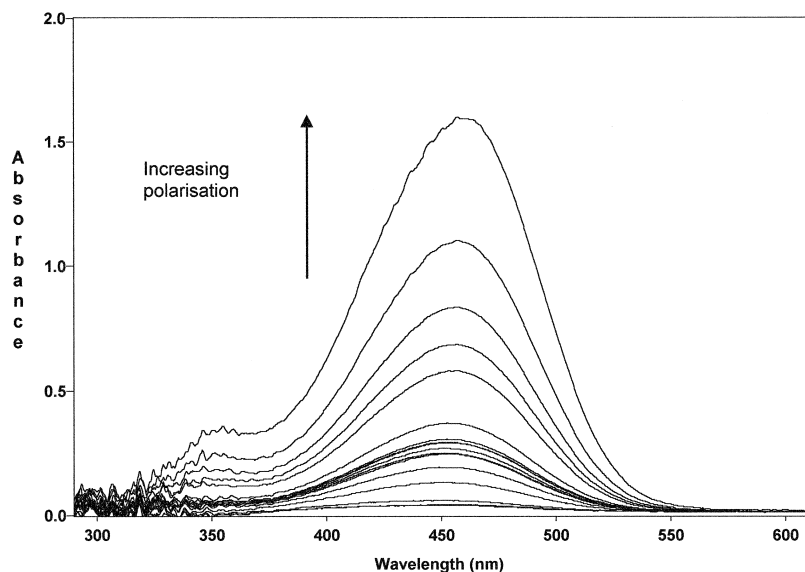


Fig. 3. Visible spectrum of TCB^- at varying applied potentials of 2.6 V to 4.3 V in 0.1 V steps.

are observed as colored species were are produced and/or consumed. At each potential, steady state concentrations of the oxidized and reduced forms of the additive (averaged across the thickness of the separator) develop. These concentrations depend upon the steady state redox shuttle current flowing at a given potential and on the diffusion coefficients for the two species. For a one-electron redox reaction, there should be a linear relationship between the steady state current and the average concentration of the shuttle species. A detailed analysis of these relationships will be the subject of a separate paper.

Tetramethylphenylenediamine (TMPD) has been found to be an effective overcharge protection additive in lithium polymer electrolyte cells, with a shuttle onset potential of about 3.2 V vs. Li/Li^+ . The spectra in Fig. 1 are those of steady state concentrations of the TMPD radical cation generated by polarizing a cell containing 0.1 M TMPD (which is only weakly colored) at increasing potentials from 0 V to 2.0 V in steps of 0.1 V. The working electrode

($\text{SnO}_2:\text{F}$) is positive. Steady-state conditions were achieved after about five minutes following each step. Although there is no reference electrode, the potential of the $\text{Li}_x\text{V}_2\text{O}_5$ counter electrode is near 2.0 V vs. Li/Li^+ at the beginning of the experiment. The absorbance increases with increasing polarization, and is a direct measure of the average concentration of the oxidized form of the additive, TMPD^+ . The absorbance at 593 nm as a function of steady state shuttle current flowing through this cell is shown in Fig. 2. An approximately linear relationship is found, with significant deviation from linearity at higher potentials, where parasitic reactions or a second ionization of the additive may take place.

Another in situ cell was constructed to measure the spectra of the radical anion of tricyanobenzene (TCBa). In this case, 0.1 M neutral TCB was added to the electrolyte. TCB is reduced at the (now negative) working electrode as the cell is polarized in 0.1 V potential steps from 2.5 V to 4.2 V in (Fig. 3). Again, the absorbance increases with increasing polarization, but the current-absorbance rela-

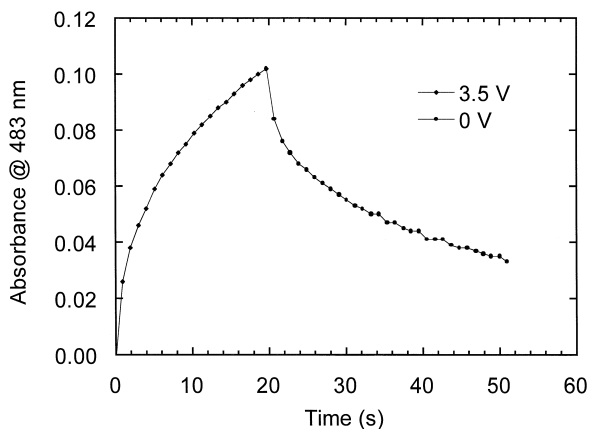


Fig. 4. TCB^- absorbance at 483 nm vs. time following potential steps at 0 and 20 s.

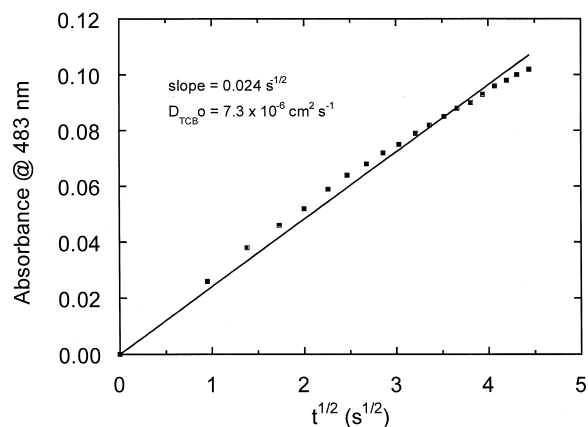


Fig. 5. TCB^- absorbance at 483 nm vs. $t^{1/2}$, 0 to 20 s.

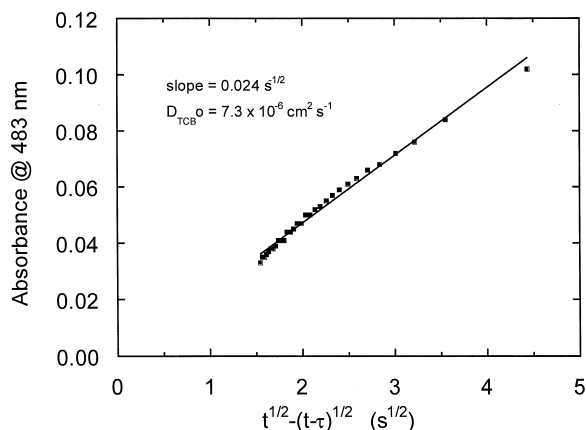


Fig. 6. TCB^- absorbance at 483 nm vs. $t^{1/2}$, 20 to 52 s.

tionship for this additive is not linear, as precipitation of some Li^+TCB^- occurs due to its low solubility in the electrolyte.

In order to determine the diffusion coefficient of the TCB molecule, a similar cell was prepared containing TCB at a concentration of 0.005 M. A single potential step of 3.5 V was imposed, and the absorbance at 483 nm was recorded at one second intervals for 20 s (Fig. 4). The potential was then stepped to 0.0 V and the decay of the anion absorbance was recorded. The increase in absorbance on polarization (Fig. 5) and the decrease on reversal (Fig. 6) have the time dependence predicted by (1) and (2), respectively [12]. Here the solubility limit for the lithium–TCB salt was not exceeded. The linearity of the data and the identity of the slopes in Fig. 5 and 6 demonstrate the stability of the anion and the reversibility of the redox reaction. From the slopes of these plots, the diffusion coefficient of the *neutral* molecule (the reacting species) was calculated to be $7.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

$$A(t) = 1.13 \varepsilon_{\text{anion}} C_0 (D_{\text{TCB}} t)^{1/2} \quad (1)$$

$$A_{\text{rev}}(t) = 1.13 \varepsilon_{\text{anion}} C_0 (D_{\text{TCB}})^{1/2} [t^{1/2} - (t - \tau)^{1/2}] \quad (2)$$

Here $\varepsilon_{\text{anion}}$ is the molar absorptivity of the TCB anion, C_0 is the initial concentration of neutral TCB, D_{TCB} is the

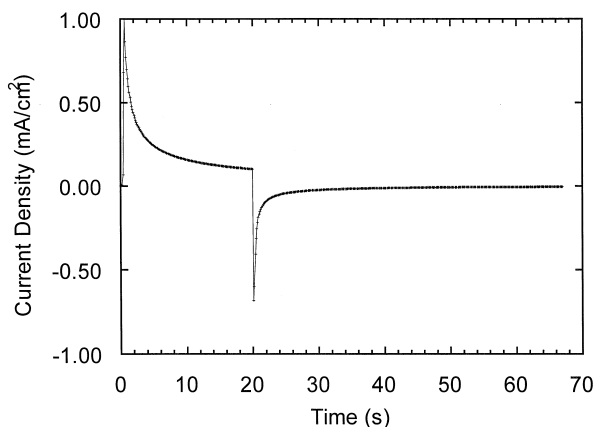


Fig. 7. Current vs. time following potential steps at 0 and 20 s.

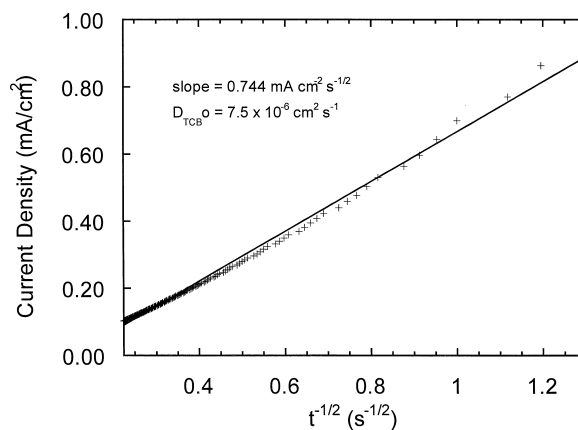


Fig. 8. Current vs. $t^{-1/2}$, 0 to 20 s.

diffusion coefficient of the neutral molecule, and τ is the duration (s) of the first potential step.

D_{TCB} may also be determined by chronoamperometry. Fig. 7 shows the current response during the experiment. The time dependence of the current is given by (3), in which n is the number of electrons carried by each shuttle molecule, F the Faraday constant, and A is the electrode area. From the slope of

$$I = 0.564 n F A C_0 (D_{\text{TCB}})^{1/2} (t)^{-1/2} \quad (3)$$

the plot of current vs. $1/t^{1/2}$ (Fig. 8), D_{TCB} is used to be $7.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, in good agreement with the spectroelectrochemical value. This shows that the cell is free of parasitic currents and that the value of n is 1.

An overall ‘effective diffusion coefficient’ for the redox pair can be calculated [1] from limiting current measurements (4), where I_s is the limiting shuttle current and d is the separator thickness. The

$$D_{\text{eff}} = I_s d / n F A C_0 \quad (4)$$

value of D_{eff} for this system is $1.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Since D_{eff} is largely determined by the smaller of the two diffusion coefficients of the oxidized and reduced forms of the additive, it is clear that the anion diffuses much more slowly in the electrolyte than the neutral molecule.

4. Conclusions

The in situ spectroelectrochemical technique described here is a simple and direct method for determining transport properties of redox shuttle overcharge protection additives for use in secondary lithium batteries. It allows us to identify the redox active species, determine the number of electrons carried by the shuttle, and quantify the diffusivity and stability of both oxidized and reduced forms. Through analysis of spectra obtained under varying conditions of potential and current density, we can also monitor the accumulation of inactive degradation products.

Acknowledgements

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