



Short communication

Influence of the solid electrolyte interphase on the performance of redox shuttle additives in Li-ion batteries – A rotating ring-disc electrode study



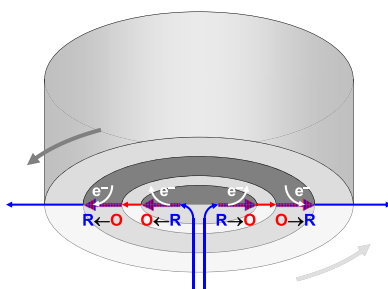
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HIGHLIGHTS

- The rotating ring-disc electrode is a powerful tool to study the reactions of redox shuttle additives.
- The presence of a SEI at the anode impedes the back-reduction of the RSA.
- The reduction behaviour of a RSA at the anode depends strongly on the characters of the RSA and the SEI.

GRAPHICAL ABSTRACT



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ABSTRACT

Redox shuttle electrolyte additives (RSAs) can be applied for reversible overcharge protection of batteries. Their successful operation involves their oxidation at the cathode and reduction at the anode. The most common anodes in lithium-ion batteries are graphite or amorphous carbon, which are normally covered with a solid electrolyte interphase (SEI). The reduction of RSAs at these anodes is in apparent contradiction with the common understanding of the SEI, which is thought to be electronically insulating. In this communication the reduction behaviour of ferrocene and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene is studied at un-filmed and SEI-filmed electrodes. It is found that it depends strongly on the type of RSA and/or composition of the SEI. The rotating ring-disc electrode (RRDE) is introduced as a powerful diagnostic tool to study the reaction mechanism of RSAs in general and the influence of the SEI in particular.

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1. Introduction

Overcharge is an abuse condition which can shorten the cycle life of Li-ion batteries (LIBs) and lead to severe safety problems [1]. As an intrinsic way of protection against overcharge redox shuttle additives (RSAs) [2] have attracted widespread interest. RSAs can

readily be added to the electrolyte and are thus less complex to apply than other overcharge protection technologies, such as e.g. external voltage regulation [3,4]. Furthermore, RSAs provide reversible overcharge protection and the battery remains operative once the overcharge conditions are removed [5]. Several classes of molecules have been investigated for their applicability as RSAs (see for instance review [3] and the references given therein, and recent original research papers [6,7]). Among the very first molecules were ferrocene (Fc) and its derivatives [2,8,9]. Unfortunately, the redox potential of Fc of approx. 3.25 V vs. Li/Li⁺ is too low for

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any of the cathode materials which are used in LIBs today. For cells with LiFePO_4 as cathode 2,5-di-*tert*-butyl-1,4-dimethoxybenzene (DTBDMB) [10–12] appears especially promising.

The general working mechanism of a RSA comprises of four steps: (i) oxidation of the reduced form of the RSA (R) to the oxidised form of the RSA (O) at the cathode: $\text{R} \rightarrow \text{O} + \text{e}^-$, (ii) diffusion of O from the cathode to the anode, (iii) back-reduction of O at the anode: $\text{O} + \text{e}^- \rightarrow \text{R}$, and (iv) diffusion of R from the anode to the cathode.

Relevant for a proper functioning are accordingly the redox potential, the reversibility of the redox process (including the stabilities of R and O), and kinetic parameters such as the diffusivities of R and O in the electrolyte. Information about these properties is commonly obtained by cyclic voltammetry (CV) or rotating disc electrode (RDE) voltammetry (e.g. Refs. [8,9,12]).

Step (iii) of the shuttle mechanism apparently contradicts the common understanding of state-of-the-art LIBs with graphite or amorphous carbon anodes, which are covered with a solid electrolyte interphase (SEI). The ideal SEI should behave like an electrolyte and be conductive for ions and insulating for electrons [13]. This raises the question how the RSA can gain electrons for the back-reduction at a SEI-filmed anode. This problem has been recognized and discussed before, e.g. by Moshurchak et al. [12] and Tang and Newman [14–16]. According to Moshurchak et al. the finding, that back-reduction of the RSA is possible even after the reduction of the electrolyte solution and SEI formation have come to an end, can be explained by differences in the electron tunnelling rate due to differences in energy of the final state (which is significantly lower for the oxidised RSA than for the solvent molecule or Li^+ ion) [12].

Tang and Newman used ferrocene as probe to study the properties and growth of the SEI by RDE voltammetry [14]. They interpreted their results based on a two-layer SEI model with a compact inner layer and a porous outer layer, incorporating a previously proposed SEI growth model based on solvent transport through the SEI [17]. Electron tunnelling can occur across the inner layer, but it is impermeable for the RSA. The outer layer is beyond the electron tunnelling range, but it is porous enough to allow selective transport of the RSA through it. Their study showed that the reduction of ferrocenium (Fc^+) is impeded by the presence of the SEI, and that the through-film reduction current can be approximately described by Butler-Volmer kinetics combined with a through-film limiting current [14].

Rotating ring-disc electrode (RRDE) voltammetry is a classical method for mechanistic and kinetic studies of electrochemical reactions. It has especially been used to investigate aqueous electrolyte systems (e.g. Ref. [18]) and lately also air electrodes in combination with non-aqueous electrolytes (e.g. Ref. [19]).

In the present work we introduce the RRDE as an ideal and powerful diagnostic tool to study the redox behaviour of RSAs. Ferrocene and DTBDMB were selected as model RSAs for the present RRDE study, since both are known to work reversibly, and since the results could be compared with the results from the previous studies mentioned above.

2. Experimental

The base electrolyte used in this study was 1 M LiPF_6 in ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 by wt.) from Ube Industries. Fc (98%) and DTBDMB (98%) were purchased from Sigma Aldrich and used without further purification.

Initial CV experiments in quiescent solution were carried out with a glassy carbon (GC) electrode (AFE2M050GC, Pine Research Instrumentation) with an area of 0.196 cm^2 and Li metal counter and reference electrodes using a scan rate of 10 mV s^{-1} .

The RRDE experiments were performed with a GC ring – GC disc electrode (custom-manufactured by Pine Research Instrumentation) with a ring area of 0.187 cm^2 , a disc area of 0.247 cm^2 , a ring-disc distance of $320 \mu\text{m}$, and a theoretical collection efficiency (η_{theo}) of 0.371. The RRDE was polished with a $0.05 \mu\text{m}$ diamond suspension (Buehler) prior to each set of experiments. All experiments were performed in a glove-box with Ar atmosphere and oxygen and water levels $<1 \text{ ppm}$ at a temperature of $24 \pm 2 \text{ }^\circ\text{C}$. Lithium metal served as reference and counter electrodes. The rotation speed of the ring-disc electrode was controlled by a rotator (Model 636A, Princeton Applied Research) between 200 and 2400 rpm. The electrochemical measurements were performed with 2 potentiostats (Versastat 4 and Versastat 3F, Princeton Applied Research) in bipotentiostat mode. The disc potential was linearly swept from an initial to a final potential at 10 mV s^{-1} , meanwhile the ring potential was kept at a constant potential and the current was recorded as a function of time. Apparent collection efficiencies (η_{app}) were calculated from the ratio of ring current (I_{ring}) to disc current (I_{disc}) using measured values from the limiting current regions [20]:

$$\eta_{\text{app}} = \frac{I_{\text{ring}}}{I_{\text{disc}}} \quad (1)$$

The concentration of RSA used in the CV and RRDE experiments was 0.01 M or 0.05 M and thus well below the solubility limits of DTBDMB (approx. 0.06 M) and ferrocene (at least 0.5 M) in the present base electrolyte. Both the CV and RRDE experiments were carried out without IR compensation.

SEI-prefilming of the ring electrode was performed by running 3 CV cycles in quiescent solution between 1.5 and 0.02 V vs. Li/Li^+ (starting at OCV) at 1 mV s^{-1} .

3. Results and discussion

3.1. CV measurements

Initially, ferrocene and DTBDMC were studied by CV in quiescent solution. The CV curves for 0.01 M ferrocene and 0.01 M DTBDMB in 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:1 by wt.) are presented in Fig. 1 and reflect the reversible redox behaviours of these two molecules. The mid-peak potentials [$E_{\text{mp}}=(E_{\text{pa}} + E_{\text{pc}})/2$] and the peak difference values ($\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$) were obtained as $E_{\text{mp}}(\text{Fc}/\text{Fc}^+) = 3.24 \text{ V}$ vs. Li/Li^+ , $E_{\text{mp}}(\text{DTBDMB}/\text{DTBDMB}^+) = 3.93 \text{ V}$ vs. Li/Li^+ , $\Delta E_p(\text{Fc}/\text{Fc}^+) = 81 \text{ mV}$, and $\Delta E_p(\text{DTBDMB}/\text{DTBDMB}^+) = 79 \text{ mV}$, with E_{pa} and E_{pc} denoting

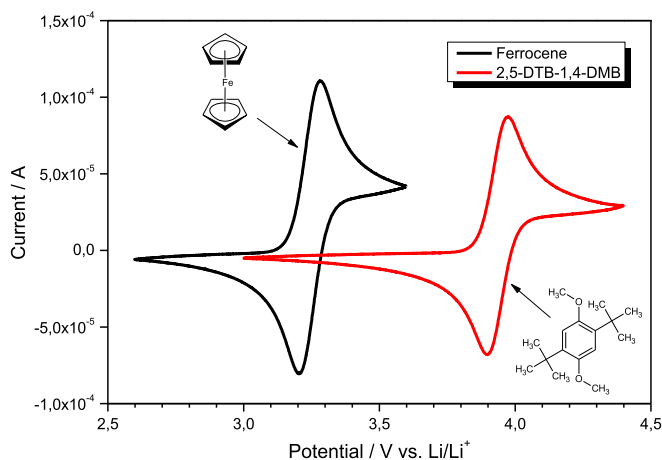


Fig. 1. Cyclic voltammograms of 0.01 M ferrocene and 0.01 M DTBDMB in 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:1 by wt.) on a GC electrode at 10 mV s^{-1} (in quiescent solution).

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