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Effects of SEI on the kinetics of lithium intercalation

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Abstract

The electrochemical stability of electrolytes at lithium, or lithium-intercalating anodes, is achieved via ionically conducting surface films termed as solid electrolyte interphase (SEI). Since the lithium deposition or intercalation process occurs on the electrode covered with the SEI, the characteristics of the SEI determine the kinetics of lithiation/delithiation, stability of the interface, and thus, the overall cell performance, especially at low temperatures. In this paper, we have reiterated the significance of the SEI characteristics over the solution properties, using a few illustrative examples from our research on low temperature Li ion battery electrolytes at JPL. The examples specifically include the beneficial aspects of a ternary carbonate mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) compared to the binary mixtures (of EC and either DMC or DEC) and quaternary solutions with appropriate co-solvents, such as alkyl esters. Published by Elsevier Science B.V.

Keywords: SEI; Lithium intercalation; Carbon anode

1. Surface films on carbon anode

The successful operation of Li-ion cells is attributed mainly to the surface films on carbonaceous anode materials. These films provide the much-needed kinetic stability to the electrolyte species even at the thermodynamically reducing anode potential. Unlike the passive films on valve metals or in primary Li cells, the anode films in Li ion cells have moderate ionic conductivity and hence are termed as the ‘solid electrolyte interface’. Understandably, the performance of the anode is dictated largely by the characteristics of SEI, i.e. its resistance, ability to prevent further electrolyte reduction, amenability to charge transfer or Li intercalation process and to some extent the diffusivity of Li⁺ ions, even though it is difficult to distinguish the slow diffusion across the SEI from the slow diffusional process within the bulk anode. The corresponding performance characteristics of Li-ion cells that are affected by the SEI include cycle life, self-discharge, rate capability and low temperature. The characteristics of the SEI depend on several factors such as the nature of the carbonaceous material and electrolyte, temperature and mode of forming the SEI (rate and temperature).

Interestingly, similar surface films are known to exist on the cathodes as well, even though their composition and properties

might be different from that of the films on the anode. In this work, however, we have focused mainly on the SEI on the carbon electrodes in different electrolytes. Nevertheless, the inference drawn from the single-electrode measurements on carbon anodes have been verified in the laboratory three-electrode cells as well as in sealed prototype cells.

2. SEI characterization techniques

Various techniques are being adopted to understand the properties of the SEI, which include direct techniques, such as FTIR by Aurbach and coworkers [1–3] for determining the constituents of the SEI, solid state ⁷Li NMR by Greenbaum and coworkers [4] for understanding the intercalated versus non-intercalated lithium, transmission electron microscopy (TEM) [5], ellipsometry, and atomic force microscopy. In addition to NMR and TEM techniques, we have adopted several electrochemical techniques. These include dc cyclic voltammetry for understanding the (kinetic) stability of the electrolyte at the anode and cathode potentials, dc micropolarization for determining the kinetics, Tafel polarization for understanding charge transfer kinetics and mass transfer effects, and electrochemical impedance spectroscopy (EIS) for determining the film resistance, charge transfer kinetics and diffusional effects. The latter technique is also used at various stages of cycling

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and storage to understand the changes in the interfacial conditions. Finally, we have made a series of capacity measurements at various rates and temperatures, especially at low temperatures to verify the improvements in the latter.

3. Low temperature electrolytes

Our research studies in the last five years at JPL, have focused on enhancing the low temperature performance of Li-ion cells, by a judicious selection of the electrolyte, especially the solvent mixture. The solvents or cosolvents need to have critical properties, such as high dielectric constant, low viscosity, adequate coordination behavior, as well as appropriate liquid ranges and salt solubilities in the medium. In addition, the chemical and electrochemical stability towards the carbon anode and the metal oxide cathode, which are controlled largely by the SEI is an important consideration. Based on these considerations, we have examined several electrolyte formulations for enhanced low temperature conductivities as well interfacial stability. A few of such systems are briefly described here.

4. Ternary versus binary alkyl carbonates

Our initial studies were based on optimizing the solvent mixtures of EC, DMC and DEC. We have made a detailed study of the EC + DMC and EC + DEC binary mixtures and the ternary, equi-proportion mixture EC + DMC + DEC, with 1 M LiPF₆ [6]. Though the electrolyte conductivity at ambient temperatures is high for the EC + DMC mixtures, the low temperature conductivity is higher for the ternary mixture. Besides, the interfacial properties in the ternary mixture are more favorable to Li intercalation–deintercalation kinetics, especially at low temperature. A comparison of the performance in the ternary and binary systems in AA cells is shown in Table 1. The film resistance increases with increasing DMC content. Also, the protective nature of the films during charge–discharge cycling or open-circuit stand is the highest in the DMC-based electrolyte, as evident from the lowest irreversible capacity, capacity fade and self-discharge. The kinetics of Li intercalation–deintercalation, on the other hand, are adversely affected at low temperature, possibly due to a contribution from the tenacious surface film. All things

considered, the ternary solvent system provides excellent low temperature performance combined with adequate durability under ambient conditions and thus constitutes a suitable baseline electrolyte for our further studies.

5. Aliphatic ester co-solvents

Our subsequent studies were aimed at further enhancing the low temperature performance via the use of co-solvents to produce electrolyte solutions from highly conducting solutions at low temperatures, but that have relatively poor filming properties by themselves. Examples of these include aliphatic esters such as methyl acetate, ethyl acetate, ethyl propionate and ethyl butyrate [7]. Aliphatic ester co-solvents improve the ionic conductivity of the electrolyte solutions, especially at low temperature, due to their favorable physicochemical properties and the effect decreases with increasing chain length or molecular weight. On the other hand, the ‘filming’ characteristic, i.e. the ability to form stable SEI for adequate kinetic protection at lithium intercalation potentials, is the least desirable for low molecular weight ester and improves with increasing chain length, as evident from the cyclic voltammetric response at the reduction potentials corresponding to lithium intercalation (Fig. 1). Accordingly, the lithium–graphite cells containing

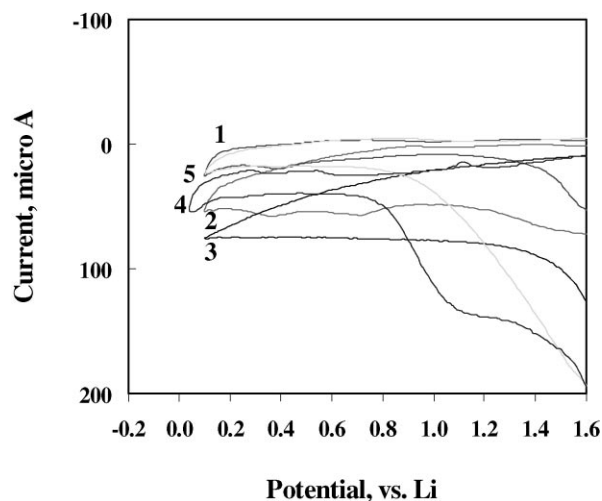


Fig. 1. Cyclic voltammetry of electrolytes containing (1) baseline (1:1:1 EC:DEC:DMC) with (2) MA, (3) EA, (4) EP and (5) EB.

Table 1

Comparison of performance with binary EC + DMC and EC + DEC solvent mixtures with the ternary EC + DMC + DEC mixture

Characteristic	EC–DMC	EC–DEC	EC–DMC–DEC
Electrolyte conductivity at low temperature	Low	High	High
Film resistance	High	Low	Intermediary
Durability (cycle life)	High	Low	Intermediary
Li intercalation kinetics at LT	Low	High	High
Irreversible capacity	Low	High	Intermediary
Self discharge	Low	High	Intermediary
Performance at LT	Low	Intermediary	High

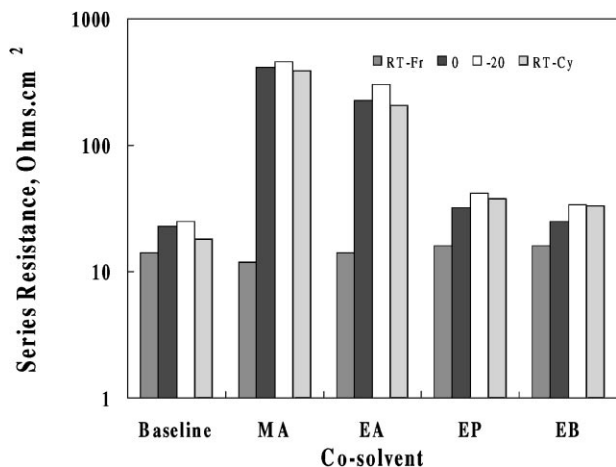


Fig. 2. Series resistance from EIS of graphite in ester based solutions at RT (F is fresh and Cy is cycled) 0 and -20°C .

electrolytes possessing low molecular weight ester co-solvents displayed higher electrode polarization and charge transfer resistance values, especially after storage/cycling (Fig. 2) and are therefore less suitable as co-solvents. Higher molecular weight acetate systems, such as ethyl propionate and ethyl butyrate, on the other hand, displayed more favorable lithium intercalation–deintercalation kinetics at low temperatures, thus, emphasizing the need for proper SEI characteristics for (enhanced) low temperature performance of lithium ion cells.

6. Pyrocarbonate additives

Also, we have used electrolyte additives (5–25%), e.g. dimethyl and dibutyl pyrocarbonates, which are expected to decompose, resulting in the liberation of CO_2 *in situ* that in turn would enable the formation of suitable SEI [8]. Fig. 3 shows the electrochemical impedance of graphite anodes (from 10^5 to 5×10^{-3} Hz) at low temperature with different electrolytes containing the pyrocarbonate additives and the baseline. As may be seen from the figure, the overall interfacial impedance, and specifically the film resistance, is considerably reduced at low temperatures with the additions of dimethyl pyrocarbonate. The prototype cells also have shown improved stability during cycling and/or storage, thus, corroborating the stability of the SEI.

In summary, we have made similar studies with several other cosolvents and additives, which similar to the above studies, reveal that the interfacial properties and the SEI

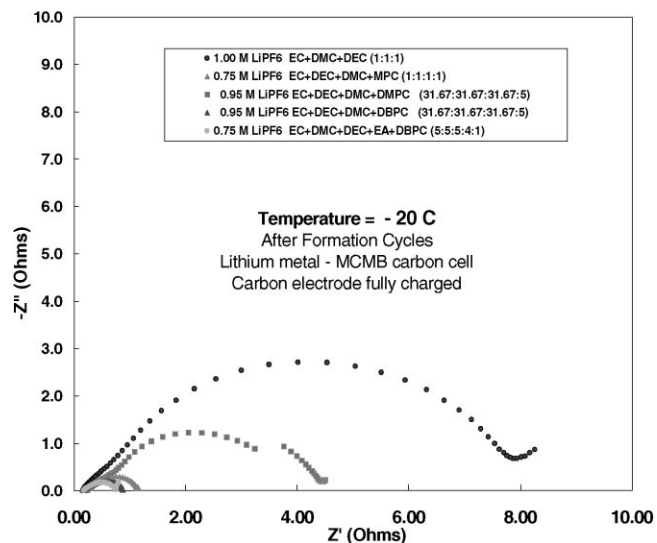


Fig. 3. EIS of graphite anode in electrolytes containing pyrocarbonates.

characteristics are as critical as, if not more than, the bulk ion migration processes in the electrolyte at low temperatures.

Acknowledgements

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