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Electrochemical Reduction of Thionyl Chloride: Solvent Effects

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Studies on the electrochemical reduction of thionyl chloride in nonaqueous media have been reported by several groups of investigators[1-4]. Experiments were run in these studies to elucidate the reduction mechanism in nonaqueous solutions containing tetraalkylammonium salts as a supporting electrolyte. Studying reduction mechanisms involved in neat thionyl chloride is difficult or impossible owing to the passivation of the electrode surface by the LiCl precipitate formed during the reduction of thionyl chloride[5-9],

$$2SOCl_2 + 4e^- \longrightarrow S + SO_2 + 4Cl^-$$

As a result, a single broad reduction cyclic voltammetric (CV) peak is observed, and extremely low currents flow beyond this peak potential. Nonaqueous solvents and non-lithium based electrolytes were used to avoid this complication. The first extensive study on the electrochemical reduction of thionyl chloride in various nonaqueous solutions was reported by Bowden and Dey[1]. They used various solvents including acetonitrile(ACN), N,N-dimethylformamide(DMF), methylene chloride(MC) and dimethylsulfoxide(DMSO). Using cyclic voltammetry(CV), coulometry and *ex-situ* UV-Vis spectroscopy, they concluded that a fairly long lived intermediate species, SO, is formed during the reduction of thionyl chloride. However, Dampier and Cole[2] ran similar experiments and concluded that there was no evidence of such an intermediate species. Later Go *et al.*[3] reported the evidence that, in dilute solutions, thionyl chloride forms an adduct with DMF molecules, *i.e.*, $SO^{2+} \cdot 2DMF$, liberating two chloride ions. Because of this species, they concluded that the first step of the electrochemical reduction of thionyl chloride in DMF can be described as

$$SO^{2+} \cdot 2DMF + 2e^- \longrightarrow SO + 2DMF$$
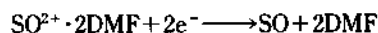
Propylene carbonate is an aprotic solvent with a moderately high dielectric constant and a wide liquid range. Many lithium salts are highly soluble in propylene carbonate.[10] It is stable toward lithium and has been one of the most widely used solvents in lithium battery research and technology.
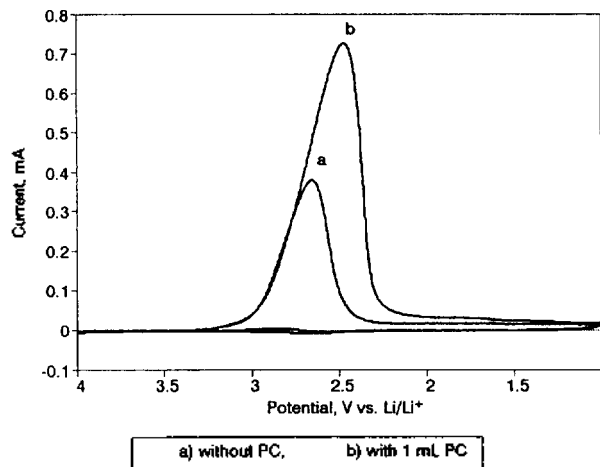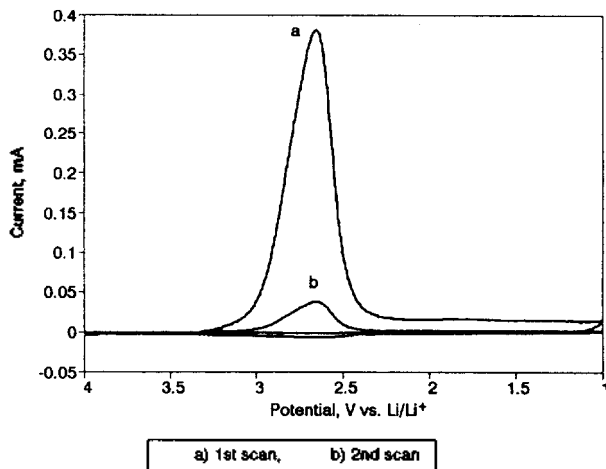

Figure 1. Cyclic voltammograms recorded from $SOCl_2$ (a) and 10% propylene carbonate-90% $SOCl_2$ (b) solution containing 1.5 M $LiAlCl_4$ as a supporting electrolyte at a scan rate of 50 mV/s.

We ran the electrochemical reduction of thionyl chloride in propylene carbonate(PC)-thionyl chloride cosolvent systems with 1.5 M $LiAlCl_4$ as a supporting electrolyte. In this experiment, a small amount of propylene carbonate was used as a cosolvent in order to evaluate its role as a cosolvent in determining the electrochemistry of the thionyl chloride reduction as well as projected current density. Here, we report the preliminary result showing how current densities are affected by $LiAlCl_4$ in the presence of a cosolvent.

An OmniSolve, glass distilled, propylene carbonate(PC) was obtained from EM Science and was used after fractional distillation under helium atmosphere at a reflux ratio of 5 : 1. Electrochemical reduction of thionyl chloride was carried out by cyclic voltammetry techniques. A single compartment cell, which housed a glassy carbon working electrode (geometric area : 0.071 cm^2), a platinum wire counter electrode, and a Li wire reference electrode, was used for the electrochemical measurements in cosolvent systems containing 1.5 M $LiAlCl_4$ as a supporting electrolyte. Thionyl chloride (Aldrich, 99.9 %), aluminum chloride (Aldrich, ultradry, 99.99%), and lithium chloride (Johnson-Matthey, ultradry, 99.995%) were used to make up a 1.5 M $LiAlCl_4$ solution. All solutions were prepared in a glove box under an argon atmosphere. A Princeton Applied Research (PAR) model 273 potentiostat/galvanostat was used for recording cyclic voltammograms.

Figure 1 shows cyclic voltammograms of thionyl chloride reduction on glassy carbon electrode. The reduction of $SOCl_2$ in the absence of PC is shown by a curve with a clearly defined current maximum i_p at the potential E_p of about 2.69 V vs. Li. Introduction of 1 mL PC into the 9 mL $SOCl_2$ leads to an increase of the maximum peak current, but the peak potential shifts toward more negative potential.

The first voltammogram recorded in a freshly prepared $SOCl_2$ shows a large current peak as shown in Figure 2. The electrochemical process is irreversible as evidenced by the lack of the reversal current. Currents observed during subsequent scans are extremely low, at about one-tenth of the original current. If, after the first scan, the electrochemical cell is left undisturbed for more than 70 minutes with the circuit open, the large CV current observed in the first

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Figure 2. Cyclic voltammograms recorded from $SOCl_2$ during the first several scans, (a) the first scan and (b) the subsequent scan. Scan rate was 50 mV/s for both cases.
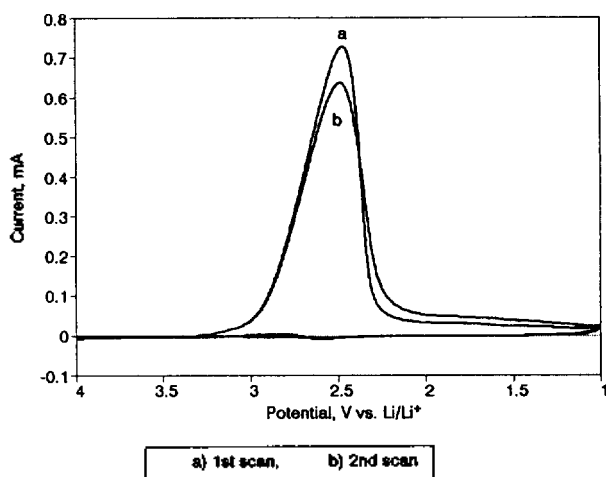
Figure 3. Cyclic voltammograms recorded from 10% propylene carbonate-90% $SOCl_2$ solution during the first several scans, (a) the first scan and (b) the subsequent scan. Scan rate was 50 mV/s for both cases.

scan is reproduced.

Figure 3 shows cyclic voltammograms in the PC-thionyl chloride cosolvent systems. The peak potential shifts toward more negative voltages and the peak current is decreased during the second voltage scan by about 15% but reproduced in about five minutes upon standing. It appears that the passivating LiCl film dissolves faster in PC-thionyl chloride cosolvent systems than in neat thionyl chloride.

We interpret this observation as indicating that the mechanism for thionyl chloride reduction is basically the same whether the reduction takes place in a neat or dilute thionyl chloride solution containing one mL PC. Also, peak potentials become more negative while peak currents increase as the concentration of thionyl chloride decreases in the PC-thionyl chloride cosolvent systems. Thus, the thermodynamics for the thionyl chloride reduction becomes less favorable, whereas its kinetics becomes more favorable. This behavior is rather unexpected in that the kinetics is improved when the concentration of the electroactive material, *i.e.*, thionyl chloride, is decreased.

In order to explain this behavior, both apparent diffusion coefficient and exchange rate constants are calculated from cyclic voltammograms (not shown) recorded at various scan rates by the methods described in previous report[11]. We can see from these results that both diffusion coefficients and exchange rate constants vary in an order of magnitude, depending on the solution composition. While the origin of variations in apparent diffusion coefficients and exchange rate constants remains unclear, the finding is significant from both practical and theoretical standpoint. One possible explanation for these observations is that the solid-electrolyte interface model[10] operates not only at the lithium anode but at the cathode as well, perhaps to a less extent. Thus, apparent diffusion coefficients and exchange rate constants may be affected by the thickness and other physical properties of the solid-electrolyte layer formed between the electrode surface and the solution. More work should be done in this area for better understanding of the phenomena described here, such as surface analysis of the film formation and dissolution.

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