

Effect of concentration of lithium ions on the voltammetric responses of nitro-substituted aromatic sulfides in dimethylformamide on glassy carbon electrodes

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Abstract

Lithium salts are used as supporting electrolytes and ion-pair forming reagents during voltammetric investigations in aprotic solvents. In the present work, these ions are found to have a significant influence on the voltammetric responses of aromatic sulfides in dimethylformamide given their concentration and the cathodic potential limits applied. At very low concentrations (< 4 mM) and cathodic potential limits (–1.4 V), lithium ions form ion-pairs with the anion radicals generated by the reduction of nitro groups on the electrode surface. This is the conventional lithium ion-pair formation effect reported in the literature. With increasing lithium ion concentration and increasing cathodic limit, the ion-pairs tend to form an insoluble salt film on the electrode surface. This leads to inhibition of further electron transfer. The inhibiting effect does not seem to correlate with the size of the reactant organic molecule involved. At cathodic potential limits exceeding –2 V, lithium ions appear to undergo direct reduction and subsequent reaction with trace levels of water in the solvent to produce a passive LiOH layer. This inhibits all further electron transfer.

Keywords: Nitro aromatic sulfides; Lithium ions; Electrode surface effects; Cyclic voltammetry; Glassy carbon electrodes

1. Introduction

The passivating effect of lithium oxide/hydroxide layers is a serious problem in all lithium batteries [1–3]. In non-aqueous solvents, however, lithium salts form ion-pairs with anion radicals. For example, it has been shown [4] that even the quinonic groups present on glassy carbon electrodes (GCE) can interact with lithium ions (Li^+) and form ion-pairs. Compounds such as quinone [5,6], nitrobenzene [6,7], anthracene [8], fluoranthrene [8] and anthraquinone [9] form more easily reducible ion-pairs with Li^+ after a one-electron reduction in aprotic solvents. Sodium ions are found to form some insoluble salt films with nitrobenzene [10] and dinitrobenzene [11] anion radicals on mercury electrodes in aprotic solvents. In these cases, the ion-pairs formed in the presence of Li^+ are found to be soluble in the solution and hence no inhibitive effects are noticed. Earlier observations of polarographic minima during the electroreduction of aromatic nitro compounds in the presence of alkali metal cations in aprotic solvents [12,13] have been attributed to the formation of electro-inactive species. Salt film formation has been noticed [14] during the electroreduction of 2,2'-dinitrobiphenyl-*x*-type compounds in dimethyl-

formamide (DMF) in the presence of lithium salts. The exact cause and conditions under which the insoluble salt films are formed have not received comprehensive attention.

During a recent investigation of the voltammetric behaviour of aromatic sulfides in aprotic solvent [15], some unusual effects of lithium salts were noticed. In addition to ion-pair formation, the formation of an insoluble film was observed at higher concentrations. At extreme cathodic potentials, even in the absence of organic compounds, passivation of the electrode surface itself was noticed. The nature of these interactions — especially the passivating effects of Li^+ ions in presence of organic redox species — are the subject of the present investigation.

2. Experimental

Dinitrobenzene, methyl-*p*-nitrophenyl sulfide and phenylmethylsulfone (Aldrich) were used as supplied. *p*-Nitrodiphenyl sulfide [16] and *p,p'*-dinitrodiphenyl sulfide [17] were prepared and purified according to the procedure described in the literature.

DMF was thoroughly purified (SISCO) immediately prior to use. AR-grade lithium perchlorate (FLUKA) was kept dry in a desiccator. All other experimental details, cells and instruments were as reported in earlier work [15]. Cyclic voltammetry was the main instrumental method [18]. All experiments were performed at 298 ± 1 K.

3. Results and discussion

3.1. Formation of ion-pairs

Ion-pair formation effects have been widely investigated on both mercury and platinum electrodes. To ensure that similarity in responses between earlier studies on these electrodes and the present investigations on GCEs ion-pair formation experiments were conducted in dinitrobenzene. The responses for this compound on GCE were found to be quite similar to those on platinum [11]. Insoluble salt film formation effects were not observed on either electrode. Aromatic nitro sulfides, however, showed significant surface effects as discussed below.

Typical cyclic voltammograms of 4 mM methyl-*p*-nitrophenyl sulfide with different Li^+ concentrations in the potential range of 0 to -1.4 V at sweep rate of 80 mV s^{-1} are presented in Fig. 1. As reported in the literature, Li^+ forms ion-pairs with the anion radical of the nitro compound which gets reduced at around -1.2 V:

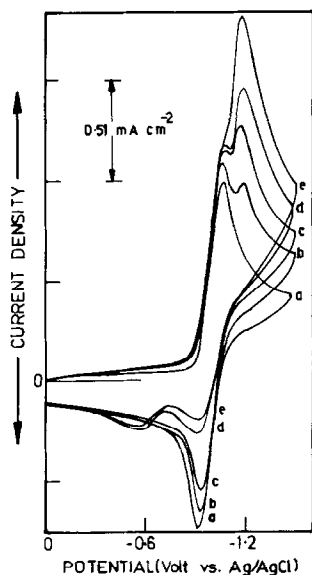


Fig. 1. Cyclic voltammograms showing the effect of Li^+ ions on ion-pair formation of the anion radical of 4 mM *p*-methyl-*p*-nitrophenyl sulfide on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$; scan range 0 to -1.4 V. LiClO_4 concentration (mM): (a) 0; (b) 4; (c) 8; (d) 11.5, and (e) 15.

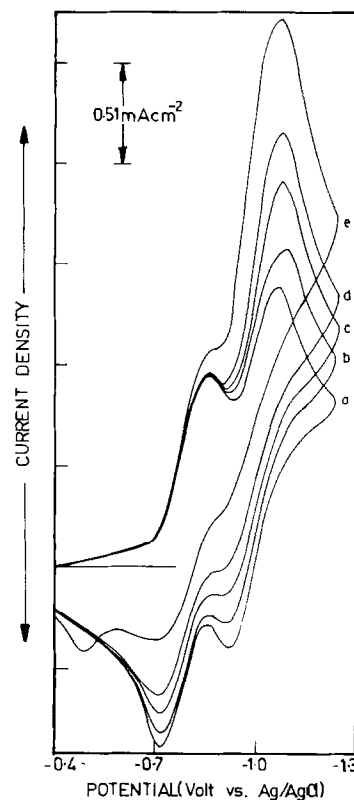
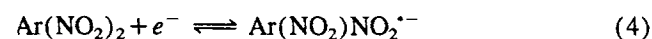


Fig. 2. Cyclic voltammograms showing the effect of Li^+ ions on ion-pair formation of the anion radical of 4 mM *p,p'*-dinitrodiphenyl sulfide on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$; scan range 0 to -1.2 V. LiClO_4 concentration (mM): (a) 0; (b) 4; (c) 8; (d) 11.5, and (e) 15.

The reduction current due to this process increases with Li^+ concentration (Fig. 1). Nevertheless, the peak potentials do not shift significantly with Li^+ concentration.

On the reverse sweep, the anodic peak due to the re-oxidation of the free anion radical of the nitro compound decreases with increasing Li^+ concentration. This is obviously due to the ion-pair formation effect cited above. At high Li^+ concentrations, a new anodic oxidation peak is observed around -0.6 V. This is probably due to the re-oxidation of the ion-pair formed between the anion radicals of the nitro compound and the Li^+ ions ($\text{ArNO}_2\text{Li}^{\cdot}$). In the case of *p*-nitrodiphenyl sulfide, Li^+ ions are also found to show similar ion-pair formation.

Slightly different voltammetric features are noticed in the case of *p,p'*-dinitrodiphenyl sulfide (Fig. 2). In this case, the first cathodic peak current is almost independent of Li^+ concentration. On the other hand, the second cathodic peak current increases significantly (Fig. 2). It appears that in the second peak potential region, formation of di-anion (due to the one-electron reduction of the second nitro group, reaction (5)) and further reduction of the lithium ion-pair (formed between Li^+ and the anion radicals generated in the first cathodic peak potential region, reaction (7)) occur simultaneously:



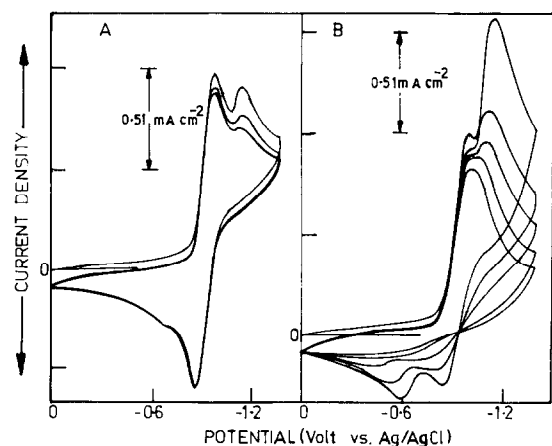
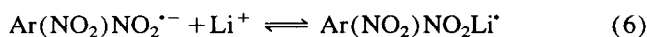
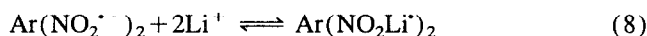


Fig. 3. Multisweep cyclic voltammograms for reduction of 4 mM *p*-nitrodiphenyl sulfide in presence of Li^+ ions on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$; scan range 0 to -1.4 V . LiClO_4 concentration (mM): (A) 4, and (B) 15.



At high Li^+ concentrations, formation of triple ions that involve a di-anion of the dinitro compound and two lithium ions may also occur, i.e.:



This is probably responsible for the absence of a re-oxidation peak due to the di-anion in the reverse sweep at high Li^+ concentrations. As in the case of mononitro compounds, a new re-oxidation peak due to the oxidation of ion-pairs is also noticed at more positive potentials.

In the lower potential region (between 0 and -1.4 V), as long as the Li^+ concentration does not exceed 4 mM, steady voltammetric responses are obtained easily in the multisweep cyclic voltammetric experiments for methyl-*p*-nitrophenyl sulfide and *p*-nitrodiphenyl sulfide (Fig. 3(A)). In the second and subsequent sweeps, a noticeable i_p decrease is observed only in the second cathodic peak potential region that corresponds to the reduction of lithium ion-pairs.

In 0.1 M tetra-*n*-butylammonium perchlorate (TBAP)/DMF system, lithium salts as such do not exhibit any reduction peak up to a negative potential limit of -2.2 V (Fig. 4(A)). In the presence of 2 mM LiClO_4 , multisweep cyclic voltammograms of 2 mM methyl-*p*-nitrophenyl sulfide do not exhibit any effects of salt film formation (Fig. 4(B)). The third cathodic peak occurs in the potential region where further reduction of the anion radical of the nitro compound occurs in the absence of Li^+ ions [19]:



where BH is the protonating agent or the solvent molecule itself. A similar voltammetric response was also obtained for *p*-nitrodiphenyl sulfide.

On the basis of all the above observations, it is concluded that lithium salts lead to soluble ion-pair formation alone during electroreduction of nitrophenyl sulfides as long as the Li^+ concentration does not exceed 4 mM and the cathodic potential limit does not exceed -2.2 V .

3.2. Formation of salt films

For the same concentration of nitrophenyl sulfide and under otherwise identical experimental conditions, significant inhibitive effects on the electrode processes are observed when the Li^+ concentration is increased beyond 4 mM. For example, the third cathodic reduction peak steadily decreases with Li^+ concentration for both methyl-*p*-nitrophenyl sulfide and *p*-nitrodiphenyl sulfide (Fig. 5). This behaviour cannot be attributed to the complete reduction of the nitro compound to ArNHOH species in the second cathodic peak potential region itself. Even at a maximum Li^+ concentration, the second cathodic peak current that appears in the presence of Li^+ increases only marginally. Only with strong protonating agents, such as benzoic acid [19], can complete reduction of

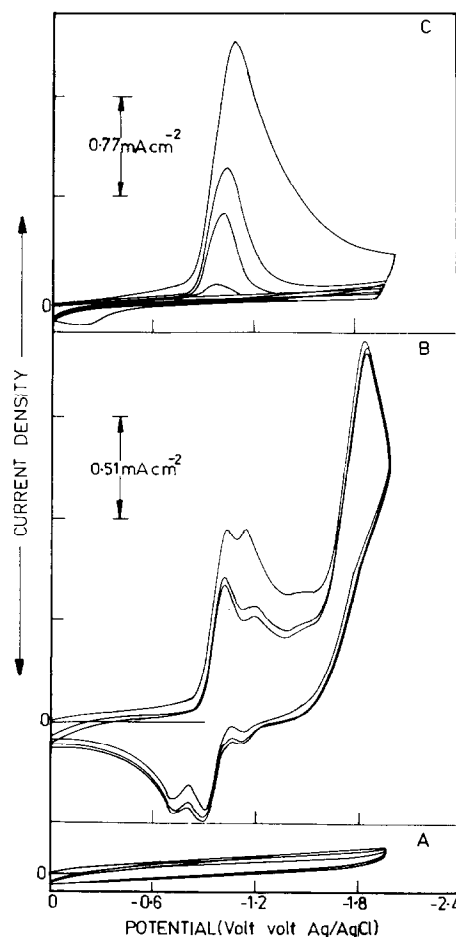


Fig. 4. Multisweep cyclic voltammograms showing the effect of Li^+ ions on reduction of methyl-*p*-nitrophenyl sulfide on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 160 \text{ mV s}^{-1}$; scan range 0 to -2.1 V . (A) 2 mM LiClO_4 ; (B) A + 2 mM methyl-*p*-nitrophenyl sulfide; (C) 2 mM methyl-*p*-nitrophenyl sulfide + 15 mM LiClO_4 .

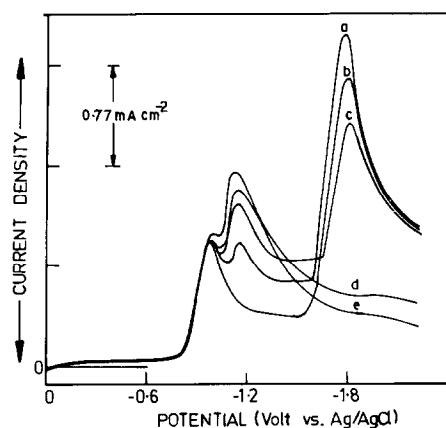


Fig. 5. Cyclic voltammograms showing the effect of Li^+ ions on reduction of 4 mM *p*-nitrodiphenyl sulfide on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$; scan range 0 to -2.1 V . LiClO_4 concentration (mM): (a) 0; (b) 4; (c) 8; (d) 11.5, and (e) 15.

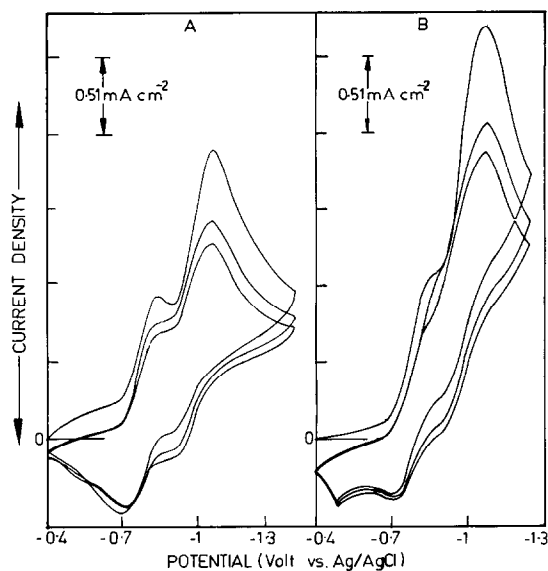


Fig. 6. Multisweep cyclic voltammograms showing the effect of Li^+ ions on reduction of 4 mM *p,p'*-dinitrodiphenyl sulfide on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$. LiClO_4 concentration (mM): (A) 4, and (B) 15.

$-\text{NO}_2$ to $-\text{NHOH}$ at less negative potentials be expected. Hence, in the present case, complete absence of a third cathodic peak when the Li^+ concentration $\geq 15 \text{ mM}$ should be attributed only to some inhibition effect.

At these high Li^+ concentration levels, multisweep cyclic voltammograms recorded with a lower cathodic potential limit also show continuously decreasing voltammetric responses with sweep numbers for both methyl-*p*-nitrophenyl sulfide and *p*-nitrodiphenyl sulfide (Fig. 3(B)).

The inhibiting effect increases significantly when the cathodic limit is increased beyond -1.4 V . Typical multisweep cyclic voltammetric responses for methyl-*p*-nitrophenyl sulfide under these conditions are presented in Fig. 4(C). It is apparent from these data that the electrode deactivation is almost complete in four cycles in the case of

methyl-*p*-nitrophenyl sulfide (Fig. 4(C)). In the case of *p*-nitrodiphenyl sulfide this type of inhibition required six cycles. Comparison of Fig. 4(B) with 4(C) shows the dependence of the inhibitive film formation effect with Li^+ concentrations under otherwise identical conditions.

All these observations suggest that some form of insoluble films are produced during the electrochemical process. One would naturally conclude that the film is due to the supersaturated ion-pairs of Li^+ and the anion radicals of nitro compounds. Higher concentrations of Li^+ , as well as more cathodic potential limits which ensure the formation of a higher concentration of anion radicals near the electrode surface, would certainly assist the formation of such supersaturated films.

In the case of *p,p'*-dinitrodiphenyl sulfide, film formation effects are noticed even at very low levels of Li^+ in the electrolyte medium. Typical multisweep cyclic voltammograms of 4 mM *p,p'*-dinitrodiphenyl sulfide in the presence of 2 mM (Fig. 6(A)) and 21.5 mM (Fig. 6(B)) LiClO_4 suggest film formation. Both the cathodic peak currents decrease continuously with sweep numbers in the potential range below -1.4 V itself (cf., Fig. 3(a) and Fig. 6(A)). Linear sweep voltammograms that demonstrate the effect of increasing Li^+ concentration on all the three cathodic peaks that cover a wider potential range of 0 to -2.2 V for this dinitro compound are presented in Fig. 7. At high Li^+ concentrations, the third cathodic peak disappears completely (Fig. 7(E)). Multisweep cyclic voltammograms that span the wider potential range at low and high Li^+ concentrations are given in Fig. 8(B) and (C); it is worth mentioning one significant difference between the salt film formation effect noticed in the case of mononitro compounds at high Li^+ concentrations in the wide potential range (Fig. 4(C)) and the dinitrodiphenyl sulfide discussed here (Fig. 8(C)). In

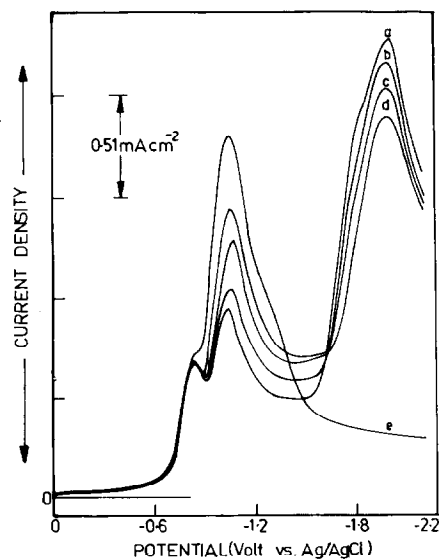


Fig. 7. Cyclic voltammograms showing the effect of Li^+ ions on reduction of 4 mM *p,p'*-dinitrodiphenyl sulfide on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$; scan range 0 to -2.1 V . LiClO_4 concentration (mM): (a) 0; (b) 4; (c) 8; (d) 11.5, and (e) 15.

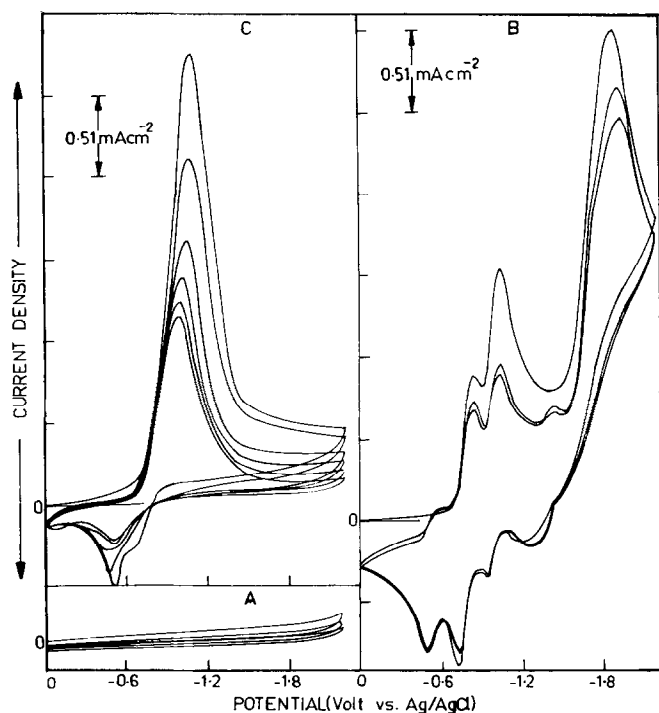


Fig. 8. Cyclic voltammograms showing the effect of Li^+ ions on reduction of p,p' -dinitrodiphenyl sulfide on GCE in 0.1 M TABP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$; scan range 0 to -2.1 V . (A) 2 mM LiClO_4 ; (B) A + 4 mM p,p' -dinitrodiphenyl sulfide, and (C) 4 mM p,p' -dinitrodiphenyl sulfide + 21.5 mM LiClO_4 .

the case of dinitro compounds, the cathodic peak currents decrease continuously with sweep number as in the case of mononitro compounds. This indicates an inhibitive salt film formation effect. Nevertheless, the cathodic peak current value does not fall to zero for the dinitro compound (Fig. 8(C)). In fact, after over ten cycles, a steady cathodic peak current is reached. In the case of the dinitro compound, the salt film that is formed is either non-compact or not completely stable. The triple ionic films thus still allow electro-reduction of nitro compounds to take place, even after a number of potential cycles. It is indeed interesting to note the higher molecular weight dinitro compound forms a salt film that is less compact than that of the lower molecular weight mononitro compound. This aspect deserves further investigation.

3.3. Formation of lithium oxide layers

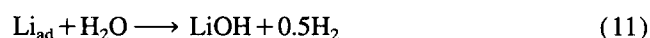
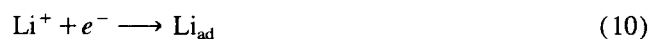
Apart from the influence of Li^+ through ion-pair and salt film formation, there appears to be another important direct inhibitive effect of these salts.

Around -2.5 V , Li^+ ions undergo direct reduction. Typical cyclic voltammetric responses of 4 mM LiClO_4 in 0.1 M TBAP/DMF systems at different sweep rates are presented in Fig. 9(A). A broad cathodic peak due to the reduction of Li^+ ions is clearly seen. This cathodic peak current also increases with Li^+ concentration up to around 11.5 mM (Fig. 9(B)). Beyond this concentration, the cathodic peak current

becomes almost independent of concentration (Fig. 9(B), curves (c) and (d)).

Even at low levels of Li^+ ions, the cathodic peak current values decrease continuously with sweep number in multi-sweep experiments (Fig. 9(C)). (Note, because of this inhibitive effect, the electrode surface had to be polished and cleaned between each voltammetric measurement shown in Fig. 9(A), (B) in order to achieve reproducibility.) At high Li^+ concentrations, the inhibitive effect becomes quite significant and in the second sweep itself the cathodic peak current completely disappears (Fig. 9(D)).

It is presumed that in these extreme cathodic potential regions, Li^+ ions undergo direct reduction and result in the formation of Li_{ad} atoms on the electrode surface. These highly active lithium atoms can react easily with trace levels of water in the solvent supporting electrolyte systems. This reaction leads to the formation of an inactive, $\text{Li}(\text{OH})$ layer, i.e.:



The effect of passive lithium hydroxide layers is an important problem in lithium batteries. The effect of such passive films on GCEs, as well as other carbon electrodes, in thionyl chloride media has been investigated [1–3]. When employ-

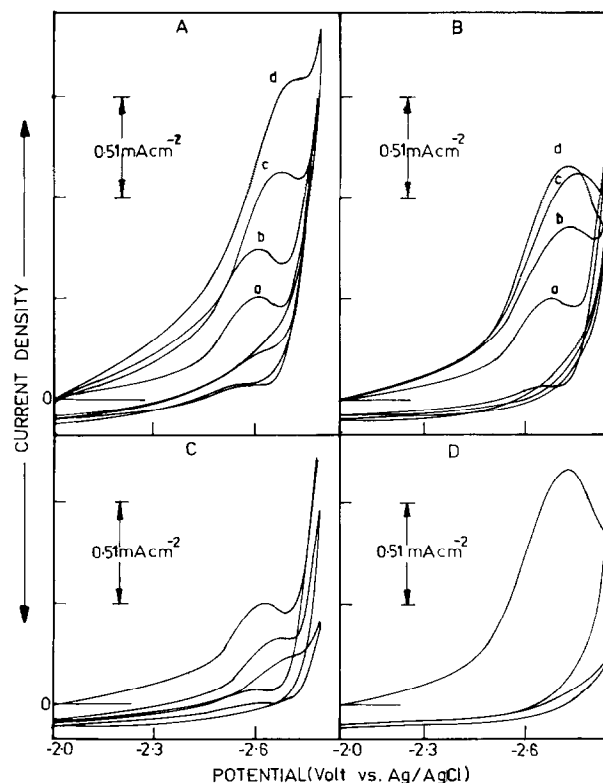


Fig. 9. Effect of sweep rate and concentration on the reduction of LiClO_4 in 0.1 M TBAP/DMF. (A) 4 mM; scan rate (mV s^{-1}): (a) 40; (b) 80; (c) 160, and (d) 320. (B) Scan rate = 80 mV s^{-1} ; LiClO_4 concentration (mM): (a) 4; (b) 8; (c) 11.5, and (d) 15. (C) Multisweep effect of 4 mM LiClO_4 ; scan rate $\nu = 40 \text{ mV s}^{-1}$. (D) Multisweep effect of 15 mM LiClO_4 ; scan rate $\nu = 40 \text{ mV s}^{-1}$.

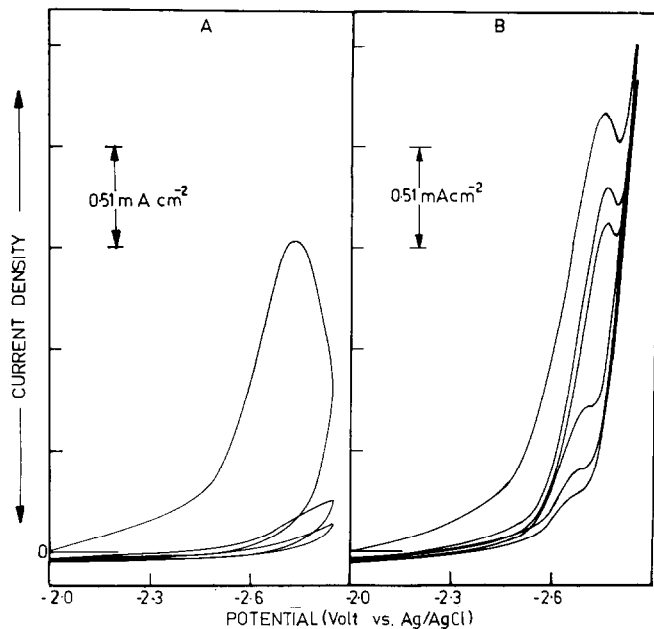


Fig. 10. Cyclic voltammograms showing the effect of water on the passive layer formed by 15 mM Li^+ in 0.1 M TBAP/DMF on GCE at scan rate $\nu = 80 \text{ mV s}^{-1}$. Water concentration (M): (A) 0, and (B) 1.

ing Li^+ ions as an ion-pair forming agent, such passivation should be taken into consideration.

An alternative explanation may be offered for the results presented in Fig. 9. If the cathodic peak current around -2.5 V is due to the formation of a lithium monolayer on the electrode surface, then very little current would be expected in the subsequent cycles unless the monolayer itself is stripped by an anodic polarization. To distinguish between these two possible explanations, the effect of deliberately added water on the multisweep cyclic voltammetric responses was examined.

Fig. 10 shows that at a sufficiently high level of water content, the cathodic process increases significantly in subsequent sweeps (cf., Fig. 10(A) and (B)). In the presence of excess water in the solvent supporting electrolyte system, the passive oxide layers can easily be solvated and hence dissolved, i.e.:



This observation leads additional support to the view that a passive LiOH layer is indeed formed on the electrode surface during cathodic reduction in the presence of trace levels water.

Fig. 11 shows the typical effects of lithium salts on the electroreduction of one of the compounds that require highly negative potentials for reduction, namely, phenylmethylsulfone. In the potential range -1 to -2.3 V , both 4 mM (Fig. 11(A)) and 12 mM (Fig. 11(B)) lithium perchlorate do not give any distinct cathodic peaks due to the reduction of Li^+ ions discussed above. The background current, however, shows a slight increase in the case of 12 mM LiClO_4 . The multisweep voltammetric responses of 4 mM phenylmethyl-

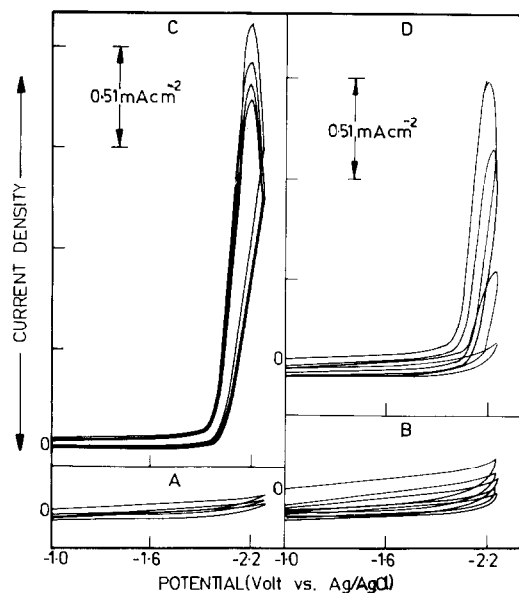


Fig. 11. Cyclic voltammograms showing the effect of Li^+ ions on reduction of 4 mM phenylmethylsulfone on GCE in 0.1 M TBAP/DMF. Scan rate $\nu = 80 \text{ mV s}^{-1}$. (A) 4 mM LiClO_4 ; (b) 12 mM LiClO_4 ; (C) A + 4 mM phenylmethylsulfone, and (D) B + 4 mM phenylmethylsulfone.

sulfone presented in Fig. 11(C) and (D) after recording the background responses (Fig. 11(A) and (B)) are indeed significantly different. The inhibitive effect is noticed during the very first cathodic peak in the presence of sulfone after polarization of the electrode in 12 mM LiClO_4 . The current also decreases drastically with sweep number.

For compounds that are usually reduced at even more negative potentials, the passivating film effect of lithium salts would thus be expected to be even more severe.

4. Conclusions

The present results on the electroreduction of nitrophenyl sulfides in the presence of Li^+ ions clearly establish three distinct modes of influence of these ions. At low concentrations of Li^+ ions (4 mM) and a low cathodic limit (-2 V), Li^+ ions interact with the anion radicals of the nitro group to form ion-pairs. These ion-pairs undergo further reduction quite close to the first cathodic reduction peak. The oxidation of the ion-pairs on the reverse sweep occurs at more positive potentials.

At higher Li^+ concentrations, formation of ion-pairs formed near the electrode surface leads to supersaturation and an insoluble salt film. Increasing the cathodic limit accelerates both the supersaturation and the formation of a totally inhibitive layer. Triple ions generated during the reduction of *p,p'*-dinitrodiphenyl sulfide promote the formation of a non-compact or unstable film. The electrode in this case does not become completely deactivated.

Beyond -2 V , Li^+ ions are reduced to form active lithium atoms. The latter can interact with trace levels of water and form passive hydroxide/oxide layers. At still higher water

levels, these films dissolve through solvation. Even in electrode processes that involve a cathodic limit of -2.3 V, the Li^+ ions exert noticeable inhibitive effects if the concentration exceeds 4 mM. During the electroanalytical measurements of such large molecular weight aromatic compounds, caution should obviously be exercised when studying the effects of lithium salts on electrode processes that involve high Li^+ ion concentrations and extreme cathodic potentials.

Acknowledgements

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