

ELECTROCHEMICAL PROCESSES IN A HIGH POWER Li-SO₂ SOURCE

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Summary

Some factors defining the specific characteristics of a high power Li-SO₂ chemical current source have been studied.

The solid-phase product of the cathodic reduction of SO₂ passivates the electrode surface, but it is gradually dissolved after de-energizing. Hence, the specific characteristics of the Li-SO₂ cell are higher on intermittent than on continuous discharge.

Perchlorate solutions have been compared with bromide solutions. The rate of the cathodic reduction of SO₂ is higher in perchlorate solutions. The range of electrochemical stability of the perchlorate solutions is wider and the cathode based on SO₂ is rechargeable.

The discharge capacity is higher in acetonitrile solutions as compared with those based on propylene carbonate. In this case the capacity increase is inversely proportional to the viscosity of the solution.

The polarization curve obtained at a porous inert cathode during the reduction of SO₂ has areas of intrakinetic, intradiffusion, external kinetic and external diffusion regions.

The anodic behaviour of a lithium electrode is determined by the properties of the film passivating its surface. Polarization resistance at anodic dissolution is practically equal to the ohmic resistance of the film. The electrochemical properties of the film are conditioned by its semiconductive nature.

Introduction

In a Li-SO₂ current source system the electrode processes are characterized by some peculiarities as compared with a current source comprised of solid cathodic active material. Cathodic and anodic active materials are in close contact with each other. The products of the cathodic SO₂ reduction accumulate on the electrode surface. The cathodic SO₂ reduction is affected by transport limitations. The polarization and discharge characteristics of the cell depend on the macrostructure of the porous inert electrode where reduction of SO₂ dissolved in the electrolyte takes place.

Experimental

Electrolytes were prepared on the basis of aprotic solvents such as propylene carbonate and acetonitrile. Lithium bromide and lithium perchlorate were used as salts. Propylene carbonate was employed after drying over CaA or NaA molecular sieves which had been precalcined for 8 h in a muffle furnace at 500 °C. The propylene carbonate was then repurified by vacuum distillation at a pressure of 4 mmHg, the temperature of the still was 96 °C and that of the vapour 91 °C. The water content of the distilled propylene carbonate was 0.004%. The conductivity of propylene carbonate measured during distillation was equal to 10^{-8} ohm⁻¹ cm⁻¹. The acetonitrile used was of "Chromatographic" grade, with 0.06% water content, supplied in ampoules. Recrystallization and vacuum drying of lithium perchlorate and lithium bromide enabled electrolytes to be obtained with a maximum of 0.02 - 0.06% water content. The preparation of the electrolytes and the electrochemical measurements were carried out in a dry box under an argon atmosphere. Dense glass filters were used for separating the electrochemical cell into three chambers: for working, auxiliary, and reference electrodes, respectively. In the working chamber the electrolyte was in excess, and the average concentration of SO₂ was constant during the measuring period.

Platinum sealed in glass (surface area 0.17 cm²), vitreous graphite embedded in fluoroplastic (surface area 0.017 cm²) and porous electrodes of carbographite composition were used for cathodes. For anodes and reference electrodes lithium rods embedded in glass tubes (surface area 0.18 cm²) were used. The lithium electrode potential gradually changes under the influence of SO₂. Therefore, the reference electrode compartment was filled with an SO₂-free background solution. Experiments showed that the peak potentials of the cathodic H₂O reduction are practically the same in both the background and the working solutions. This suggests that the diffusion potential at the background and working solution interface is low and may be neglected.

Results and discussion

Cathodic reduction of SO₂ in a solution based on LiClO₄

Figure 1 shows potentiodynamic curves on a platinum electrode in 1M LiClO₄ with PC background solution, and 1M LiClO₄, PC, and 2.2M SO₂ working solution. The peak for the cathodic reduction of SO₂ is observed at a potential of 2.6 V, the potential sweep rate being 80 mV/s. The reverse run of the curve exhibits two peaks for the oxidation of reduction products in the anodic region. It should be noted that in the case of a vitreous graphite electrode there is only one peak in the anodic region. The same shape of curve was obtained in tetrabutyl ammonium perchlorate, dimethylformamide and SO₂ solutions as reported in ref. 1.

The potential differences between the cathodic and anodic current peaks are dependent upon the conditions under which the curve was ob-

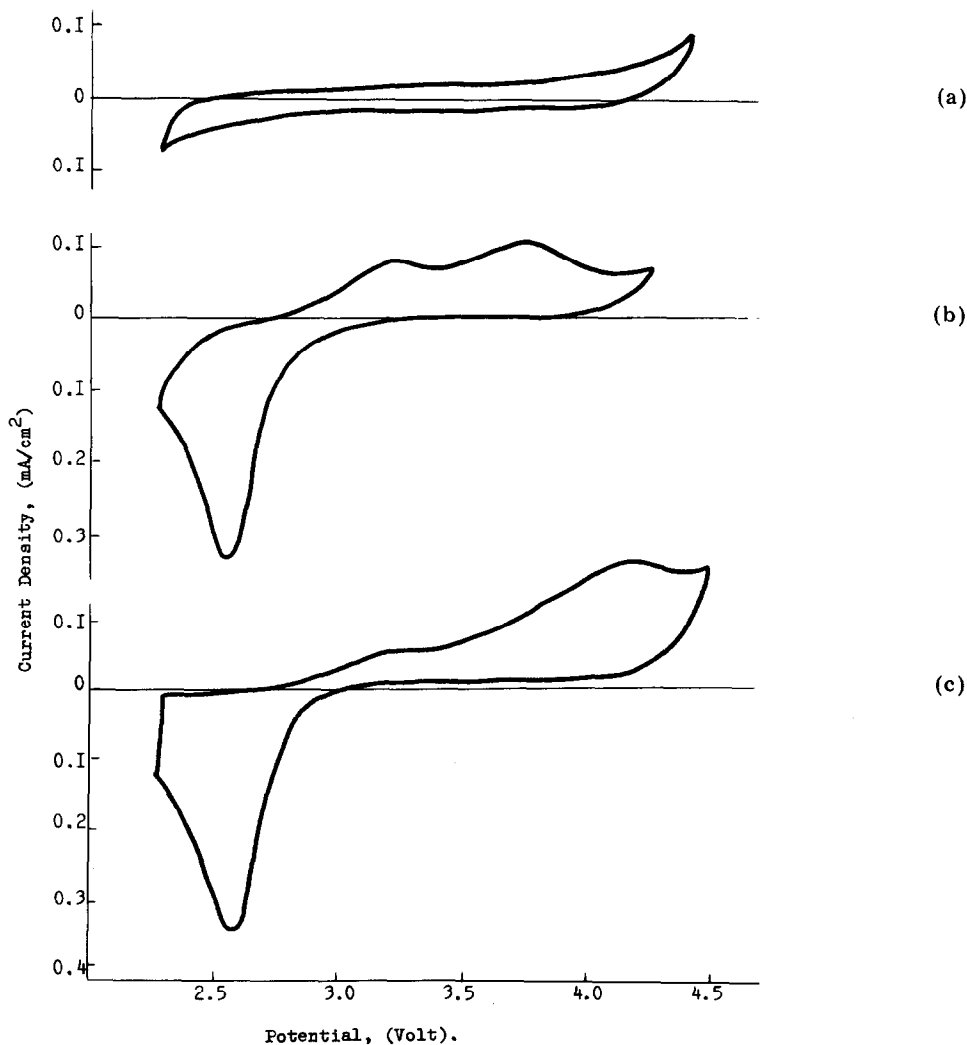


Fig. 1. Potentiodynamic curves on a platinum electrode: (a) in PC, 1M LiClO₄ background solution; (b) in PC, 1M LiClO₄, 2.2M SO₂ working solution; (c) the electrode was held for 3 min at 2.2 V after measuring curve (b).

tained. The more negative the reverse scanning potential, the higher the more positive anodic peak on the platinum electrode. At the same time, the anodic peak shifts toward more positive potentials, *i.e.*, the overvoltage of the anodic process increases. On galvanostatic cycling the deeper the cathodic polarization, the longer the plateau on the anode curve, which is shifted to more positive potentials. Similar dependences are known for the process of producing metal amalgams [2]. It follows that the product of the electrode reaction accumulates on the electrode surface during the cathodic reduction of SO₂ from lithium salts in propylene carbonate solutions. With a decrease

in the potential sweep rate the ratio of the second anodic peak (more positive) to the first one increases. The first anodic peak will decrease and the second one will increase if, after taking the cathodic branch of the curve, the electrode is held at a steady cathodic potential (e.g., 2.2 V) and then the anodic branch of the curve is plotted as a potentiodynamic curve. This proves that the first anodic peak corresponds to the anodic oxidation of an intermediate product of the cathodic SO_2 reduction which, during chemical reaction, changes to the end product, lithium dithionite precipitating on the electrode surface (Fig. 1, curve C).

When deposited on the electrode surface, the product of the cathodic reduction of SO_2 inhibits further process. After de-energizing, the electrode surface is gradually regenerated due to dithionite dissolution. For example, after the cathodic reduction of SO_2 on a smooth platinum electrode, $i = 0.07 \text{ mA/cm}^2$ in 1M LiClO_4 , PC, 2.2M SO_2 electrolyte, the electrode surface was regenerated for 40 min to such an extent that on repeated discharge the cathodic capacity reached 75% of its initial value.

Owing to the partial dithionite solubility the effective capacity of a current source depends upon the discharge regime of the cell. The discharge capacity of a cell discharging at regular intervals which provides dithionite dissolution is higher than the discharge capacity of the cell under constant load. A D-size Li- SO_2 cell with an initial 1.8M LiBr electrolyte mixed with PC and AN in the ratio 1:3.3 and an SO_2 concentration of 60% has been investigated. In the case of a constant 0.5 A discharge the cell yielded 5.8 A h at 2.7 or 2.6 V average discharge voltage. At the end of discharge the voltage drops to 2.0 V. With a daily interval the cell has been discharged to a total capacity of 7.3 A h and the recovery of active cathodic material was 75%.

The active cathodic material, SO_2 , is dissolved in the electrolyte, therefore the cathodic process may be generally limited not only by passivation of the surface with a solid state reaction product, but also by diffusion limitations of reagent transport to the electrode surface. The decisive influence of one of these factors depends upon the process parameters. Figure 2 shows, in Sand's coordinates, the results of galvanostatic measurements. Evidently, the relation obtained may be regarded as diffusion controlled only at high current densities. At low currents this value is far less than could be predicted from diffusion limitations. Under these conditions the electrode surface is affected by passivation with solid reaction product before the diffusion limitations occur.

The SO_2 concentration in an actual current source is high. Diffusion limitations occur either at the end of discharge as the active material concentration decreases, or within a porous electrode because of considerable hindering of the transport process through the liquid phase in the pore space.

Comparison between perchlorate and bromide solutions

A comparison between perchlorate and bromide solutions used as electrolytes in an Li- SO_2 current source showed the following: SO_2 solubility is

higher in bromide electrolytes compared with perchlorate electrolytes. For instance, at 25 °C, 0.7 moles of SO₂ per 1 mole of a solvent is dissolved in PC, 1M LiClO₄ electrolyte, but 0.8M/M in PC, 1M LiBr, 0.5M/M in AN, 1M LiClO₄ electrolyte, 0.6M/M in AN, 0.7M LiBr. The higher solubility of SO₂ in bromide solutions is a result of the better solvation by SO₂ molecules of halogen ions as compared with the solvation of perchlorate ions [3].

The conductivity of perchlorate solutions free from SO₂ is higher than that of bromide solutions. However, when SO₂ is dissolved in the solutions, the conductivity of bromide solutions changes more sharply and becomes higher than that of perchlorate solutions.

The limit of electrochemical stability of both bromide and perchlorate solutions is practically the same in the cathodic region. At about 1.0 V potential against the lithium reference electrode the formation of an alloy of platinum with the reducible lithium begins.

Within the range of anodic potentials the limit of electrochemical stability of bromide non-aqueous electrolytes is nearly 1 V less than that of

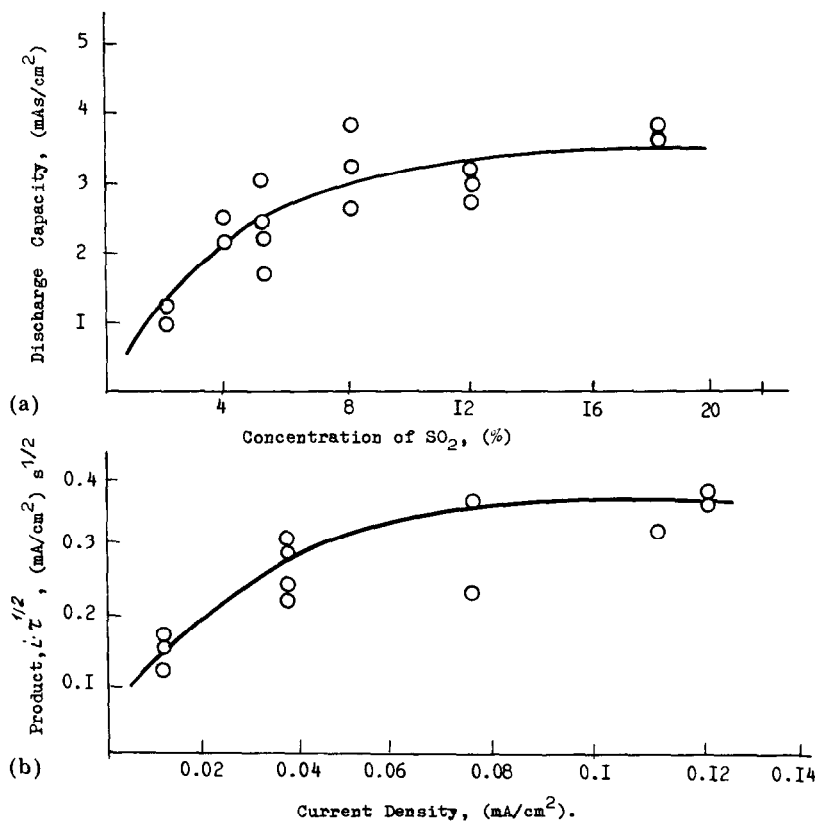


Fig. 2. The influence of SO₂ concentration (a) and current density (b) on the galvanostatic cathodic characteristics of the platinum electrode: (a) current density 0.035 mA/cm²; (b) SO₂ concentration 2.2M.

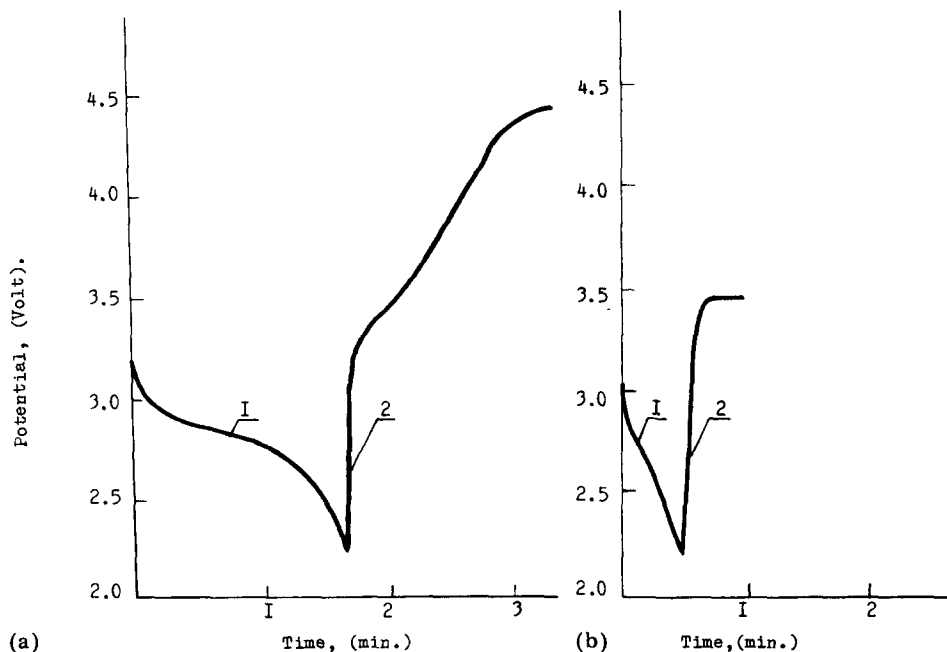


Fig. 3. Galvanostatic cathodic (1) and anodic (2) curves on a platinum electrode in (a) PC, 1M LiClO₄, 2.2M SO₂ solution and (b) PC, 1M LiBr, 2.2M SO₂ solution. Current density 0.058 mA/cm².

perchlorate electrolytes. At a potential of 3.5 V the electrochemical oxidation of Br⁻ ions to free bromine begins. The bromine produced reduces at a potential of 2.45 V.

The cathodic SO₂ reduction is considerably hindered in bromide solutions as compared with perchlorate solution (Fig. 3). As oxidation of the bromide electrolyte begins at less positive potentials than those for the oxidation of the products of the cathodic reduction of SO₂, the SO₂-based cathode cannot be recharged in bromide electrolytes.

The cathodic reduction of SO₂ from perchlorate electrolyte in acetonitrile solutions gives a longer discharge than in propylene carbonate solutions (Fig. 4). This is due to the influence of electrolyte viscosity on SO₂ diffusion. In bromide solutions the influence of propylene carbonate and acetonitrile solvents is manifested to a smaller degree. In this case the salt has a decisive influence, but not the solvent.

Cathodic reduction of SO₂ on porous electrodes

In a Li-SO₂ current source porous electrodes are used as an inert cathode where the SO₂ is reduced. The investigations showed that the dependence of discharge capacity on SO₂ concentration and current density is the same for both smooth and porous electrodes. Plotting a stationary polarization curve for the process of cathodic reduction of SO₂ on a porous elec-

trode is impossible, as an insoluble product precipitates and the electrode structure changes during discharge. Figure 5 shows a galvanodynamic curve at 0.2 mA/s sweep rate. Four parts are observed on the curve.

(a) A region of intrakinetic limitation, defined by the microkinetics of the electrochemical process on the inner surface of the pores.

(b) A region of intradiffusion limitations defined as the difficulties of transferring the active material dissolved in the electrolyte into the pore space of the electrode.

(c) A region of external kinetic limitations. At these current densities the process is almost completely displaced to the external surface, the elec-

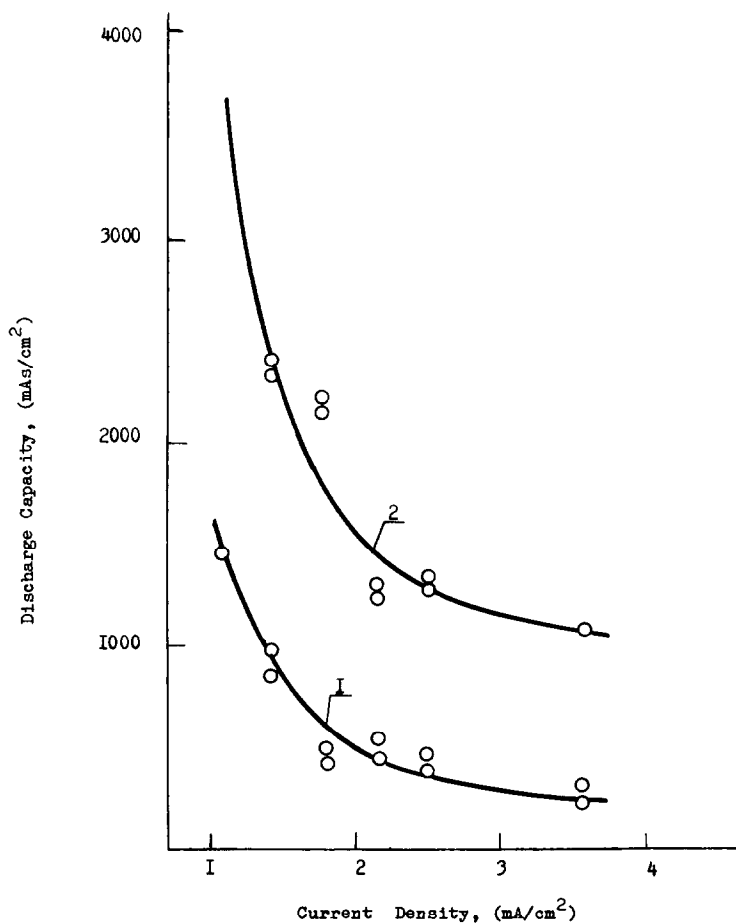


Fig. 4. The influence of current density on the discharge capacity for SO_2 cathodic reduction on a low-porosity graphite electrode. Electrolyte: 1, PC, 1M LiClO_4 , 2.2M SO_2 ; 2, PC:AN (1:1), 1M LiClO_4 , 2.2M SO_2 .

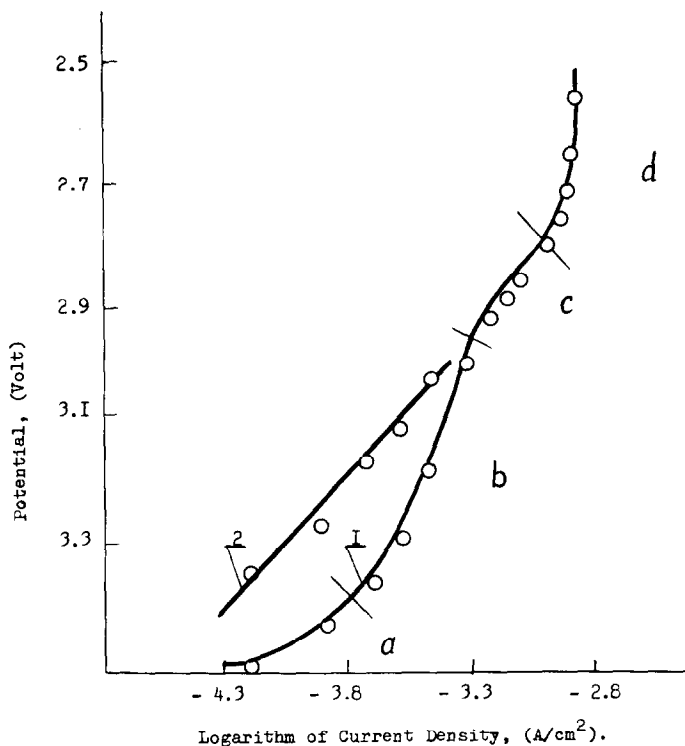


Fig. 5. Polarization curve of sulphur dioxide reduction on a low-porosity graphite electrode: 1, on a fresh electrode; 2, on a pre-used electrode.

trode operates as a smooth one and the slope is halved according to porous electrode theory [4].

(d) A region of external diffusion limitations where the process is inhibited by SO_2 diffusion to the external surface of the electrode.

The polarization curve on the pre-used electrode was shifted to more negative potentials. The slope plotted on ϕ - $\lg i$ coordinates is considerably less than that on a fresh electrode because of dithionite deposition within the electrode pores, which results in a decrease of porosity. The experiments showed that a change in the macrostructure of a porous electrode may considerably increase its discharge capacity.

Electrochemical behavior of the lithium electrode

The electrochemical behavior of a lithium electrode was investigated in a lithium perchlorate solution in propylene carbonate and also in a lithium bromide solution in propylene carbonate.

An interaction between Li and the solution results in the formation of a passivating film on the electrode surface. The resistance of this film deter-

mines the behavior of the lithium electrode on anodic polarization. The value of the film resistance was calculated using the experimental data obtained by three methods.

Making use of the galvanostatic curves, the value of the initial potential jump of the electrode was estimated, depending on the time the electrode had been in the solution and on the value of the anodic current. Practically, the initial jump of the potential is a linear function of the polarization current.

From the galvanodynamic characteristics, the slope of the polarization curve over its initial linear portion was determined. The polarization resistance calculated from the initial portion of the galvanodynamic curve is in good agreement with the resistance calculated from the galvanostatic measurements.

The ohmic component of the Li electrode potential was also measured using the curves obtained from current interruption measurements. In this case a relay was included in the polarization circuit. The response frequency was chosen so that the properties of the film would not change during the measurement period. The coincidence of the direct and the return run of the $\Delta U-i$ curve confirms the invariable nature of the film properties. The ohmic component of the Li electrode potential measured in such a way is in good agreement with the galvanostatic and galvanodynamic measurements.

The investigations carried out show that the polarization resistance on the anodic dissolution of Li depends on the ohmic resistance of the film covering the electrode surface. To control the change of a film resistance depends on periods of time. Then galvanostatic, and galvanodynamic measurements, and cut electrode was immersed into the electrolyte and held in it for various periods of time. Then, galvanostatic, and galvanodynamic measurements, and those for current interruption curves were carried out. Each measurement was made on a freshly prepared electrode.

A passivating film is formed on a freshly cut electrode as soon as it is immersed into a non-aqueous electrolyte. The film has a resistance of 18 ohm cm^2 in PC, 1M LiClO_4 solutions. In a bromide solution it is less, some 7 ohm cm^2 . The film resistance gradually increases on an electrode immersed in a non-aqueous electrolyte. For example, in 24 h the resistance increased up to 64 ohm cm^2 and 12 ohm cm^2 in perchlorate and bromide solutions, respectively. Br^- ions are known to be good depassivators for aqueous solutions. In this instance the influence of Br^- ions may be attributed to their adsorption on the electrode surface. This effect hinders the interaction between Li and the solution.

The film formed on the surface of an Li electrode is inherently semi-conductive. This is reflected in the impedance measurements (Fig. 6). The capacity of the film decreases considerably with a.c. frequency and with Li electrode "ageing". At a relatively low frequency the capacity of the film is determined by space charge and surface states. At high frequencies it is mainly determined by the space charge which relaxes more quickly than the surface levels.

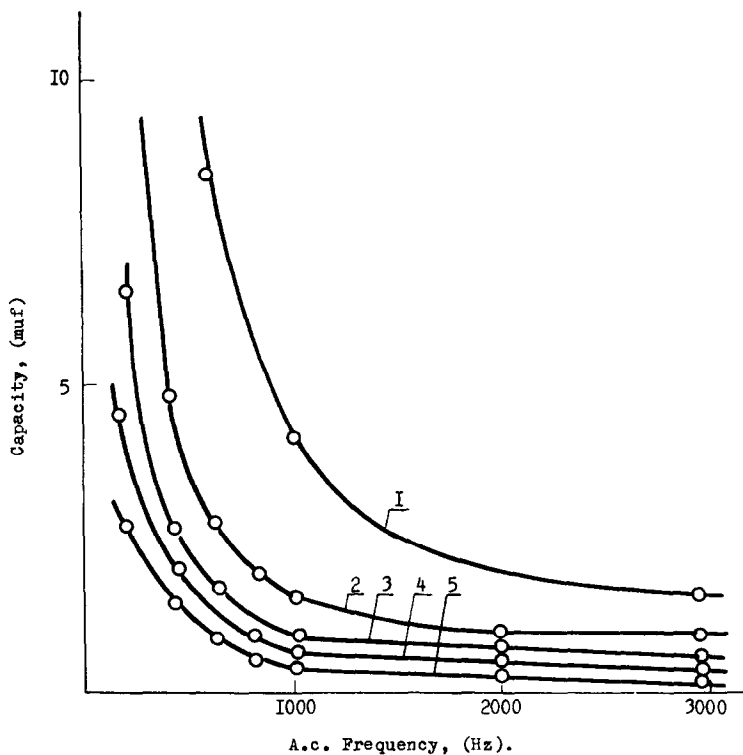


Fig. 6. The relation between capacity measured on a lithium electrode in PC, 1M LiClO₄ solution and a.c. frequency. The electrode was held in the solution for: 1, 10 min; 2, 24 h; 3, 48 h; 4, 96 h; 5, 144 h.

Conclusions

In the cathodic reduction of SO₂ from solutions based on propylene carbonate the reaction has two steps. In the electrochemical reduction, a product is obtained which then changes into lithium dithionite, *i.e.*, the end product of the chemical reaction. The end product precipitates on the electrode surface and passivates it. After de-energizing, the solid-phase product is gradually dissolved and the electrode surface is regenerated. Therefore, the discharge capacity is higher in the case of an intermittent discharge of an Li-SO₂ cell than in the case of a constant current load.

Perchlorate solutions have certain advantages over bromide solutions. In such solutions the rate of the cathodic reduction of SO₂ is higher.

Due to the wide range of electrochemical stability of perchlorate solutions the cathode, based on SO₂, may work as a rechargeable cathode.

In the cathodic reduction of SO₂ at a porous electrode the controlling stage of the reaction depends on the current density. The electrode may

operate in intrakinetic, intradiffusion, external kinetic, and external diffusion regions.

The polarization resistance on the anodic dissolution of Li is practically equal to the ohmic resistance of the passivating film which is formed on its surface. The electrochemical properties of the film are determined by its semiconductive nature.

References

- 1 F. Magno, G. A. Mazzocchin and G. Bontempelli, *J. Electroanal. Chem.*, 57 (1974) 89 - 96.
- 2 Z. Galus, *Theoretical Principles of Electrochemical Analysis*, Mir, Moscow, 1974, p. 552.
- 3 T. Baddington (ed.), *Non-aqueous Solutions*, Khimija, Moscow, 1971, p. 373.
- 4 O. S. Ksenzhek, *Electrochim. Acta*, 9 (1964) 629.