STUDY OF A LITHIUM–LITHIUM PROPIONATE ELECTRODE IN PROPYLENE CARBONATE

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Summary

Preliminary data are presented on the electrochemical behaviour of a secondary lithium electrode in propylene carbonate at 25 °C. The anion of the insoluble lithium propionate salt, whose precipitation is favoured by the anodic dissolution of lithium, was introduced into the solvent as a tetrabutylammonium salt. This was prepared by neutralising tetrabutylammonium hydroxide with an excess of propionic acid followed by vacuum evaporation to remove the unwanted water. The introduction of this salt into the solvent increases its specific conductivity without affecting its compatibility with lithium. All measurements were made with freshly prepared mercury–mercurous propionate reference electrodes to overcome problems involving their stability over prolonged periods.

Steady-state potentiostatic polarization curves, anodic galvanostatic, and cyclic voltammetry measurements provided information on the kinetics of the lithium system. It was shown to be reversible, provided that the overpotential does not exceed 60 mV, and may be able to deliver current densities of the order of 0.25 mA/cm^2 without appreciable polarisation.

Consideration of the reduction of the electrolyte on platinum and lithium electrodes is also discussed.

1. Introduction

Communication units, air borne power units, missiles, space vehicles and other equipment used in defence and civilian applications require batteries possessing very high gravimetric and volumetric energy densities in order to replace heavy lead–acid, nickel–cadmium or other conventional systems. The technological requirements in many of these applications are so stringent and indispensable that other factors such as cost become secondary.

Of the primary systems, lithium batteries possess considerably higher energy densities (150 - 300 W h/kg) than conventional aqueous batteries (90 - 130 W h/kg). Moreover, they have good charge retention due to the passivation of the lithium anode by the electrolyte solution. In the case of

secondary lithium systems, however, a key technical problem, the unsatisfactory cycling behaviour of the secondary lithium electrode at normal temperatures remains, although their technology has been actively pursued for more than 20 years [1 - 4].

While lithium may be plated onto a conducting substrate from a variety of organic electrolytes with 100% efficiency [5], subsequent stripping is invariably less efficient [5 - 7]. After each cycle an increased amount of lithium is prevented from further dissolution and this leads to rapid cell failure.

A wide variety of innovative strategies has been developed within the last 4 years in an attempt to solve this problem: these are adequately reviewed by Koch [7]. Here we consider a novel approach to the improvement of the cycling efficiency of the negative electrode; replacement of lithium with a second kind of electrode. Electrodes of this second kind are common in aqueous batteries but are not used in silver zinc cells and this may explain the poor performance of this system.

Our approach to this problem has been to develop an electrode of the type $Li/LiX/X^-$, where LiX represents an insoluble lithium salt and X^- its anion. The anion of the insoluble salt, whose precipitation is favoured by the anodic dissolution of lithium, is introduced into the solvent as a tetrabutylammonium salt. Propylene carbonate has been employed because of its stability *vs.* lithium [7]. It was found that the propionate–propylene carbonate electrolyte system is experimentally a very difficult field and, for example, we have not been able to define the system adequately with respect to interferences from water. A reference electrode was developed, however, which, while not perfect, was satisfactory if used immediately after being prepared and long-run experiments avoided. Moreover, apart from Caiola's papers on similar electrodes [8 - 11], this type of system has never been studied electrochemically in organic electrolytes, and this stimulated the present publication.

2. Experimental

2.1. General

Most of the procedures and the electrochemical experiments were conducted at normal temperature (25 ± 1 °C) in a dry box under nitrogen atmosphere.

2.2. Materials

Due to the preliminary nature of this work, propylene carbonate (PC) (Merck for synthesis), tetrabutylammonium hydroxide 0.1N (TBAOH) (Merck, dissolved in propanol–2/methanol), propionic acid (PrH) (Merck for synthesis, 99%), lithium chloride (Fisons, analytical reagent, dried), mercuric oxide (Merck, highest purity available) and acetone (Merck for analysis, 99.5%) were used without further treatment.

2.3. Electrolyte preparation

Electrolyte solutions were prepared by dissolving tetrabutylammonium propionate (TBAPr) in propylene carbonate. This procedure was followed by drying and stirring for 24 h with freshly activated Linde 5A molecular sieves. These dry procedures are accepted as being rudimentary and the use of molecular sieves on solutions containing $Li^\oplus$ could result in ion exchange with Na^+. Karl Fischer analysis, however, showed that solutions so dried contained less than 100 ppm H_2O, while untreated solutions contained approximately 1200 ppm, and this result gave us some confidence in the procedure adopted.

Preparation of the ammonium salt, used as a solute, was carried out by neutralising TBAOH with an excess of PrH (pH $\cong$ 6.5), followed by vacuum evaporation ($\cong$ 5 mmHg, for three days) at 50 °C to remove most of the unwanted water. White crystals of TBAPr were obtained after allowing the resulting viscous liquid to cool for several hours at —15 °C.

2.4. Electrode preparation

The working electrode was constructed by plating Li onto a 1 cm wide, 0.5 mm thick, metal foil. Lithium electrodeposition was conducted in an H-type cell, the two compartments being separated by a glass frit.

Initially, a solution of 5×10^{-2}M/l LiCl in propylene carbonate electrolyte was used in conjunction with two electrodes prepared from platinum foils attached to platinum wires (Johnson Matthey and Co. Ltd.). Lithium was electrodeposited from this electrolyte at a constant current density of 1 mA cm^{-2} without any sign of gas evolution or side reaction. Prolonged deposition was, however, necessary to increase the thickness of the Li deposit, but this led to the formation of Li dendrites. At current densities between 2 and 10 mA cm^{-2} gas was evolved and the deposits became impure and mossy.

Much better deposits were obtained by using acetone in place of propylene carbonate, but adherence to the Pt cathode was poor. These deposits were white immediately after plating but became increasingly dark on open circuit stand. Using nickel (99.5% purity, GoodFellow Metals) as the cathode material, current densities between 5 and 10 mA cm^{-2} could be applied without secondary reactions and deposits up to 0.5 mm thick were obtained as a grey, metallic coating which was more adherent and coherent than previously. The final working electrode was made from electrodeposited Li on Ni, using LiCl + acetone as electrolyte. It was stored in acetone and before use was thoroughly washed in pure propylene carbonate and anhydrous hexane.

To prepare the reference electrode, mercurous propionate (Hg_2Pr_2) and a little ultrapure mercury were ground to a paste in a mortar with 0.1M TBAPr solution. The remaining TBAPr solution required to fill the electrode vessel was previously stored over a little Hg_2Pr_2 in order to saturate the solution.

Mercurous propionate was prepared by precipitating it from a well-mixed mercuric oxide–mercury paste on addition of PrH. The white precipitate was washed thoroughly under suction with N/2 PrH solution and dried over anhydrous calcium chloride.

To ensure that this precipitate was mercurous propionate and not mercuric propionate, a sample of the prepared white powder was added to a few ml of distilled water. Negligible dissolution occurred when the solution was agitated. A few drops of HCl were then added to an aliquot of the supernatant limpid solution and an immediate precipitation of mercurous chloride was observed. X-ray diffraction also confirmed that the white powder was Hg_2Pr_2.

The counter electrode comprised a large platinum sheet separated from the main cell compartment by a frit, to avoid contamination by the reaction products at this electrode.

2.5. Cell assembly

A glass cell of standard design was used to perform the polarization experiments. The electrodes were fixed in position in the cell by means of ground glass joints; the reference electrode was separated from the working electrode by a Luggin Capillary.

2.6. Conductivity measurements

The specific conductance of the electrolyte solutions was measured with a 4959 Leeds and Northrup bridge employing a conductivity cell equipped with Pt electrodes and having a constant of 0.503 cm^{-1}. A starting solution of 1M TBAPr was progressively diluted and the corresponding conductivities were measured after thermal equilibration.

2.7. Solubility and compatibility tests

The solubility of the lithium propionate (LiPr) was measured by anodically oxidizing lithium at a constant current density of 4 mA cm^{-2} for about 200 min in a solution of TBAPr in PC (0.1M). Subsequently, the solution was stirred and equilibrated with the electrode system for one week. An aliquot of the supernatant solution was then collected and the LiPr solubility calculated by determining the Li^+ content.

To test compatibility, Li electrodes were immersed in the electrolyte for several weeks and a visual inspection of the electrode/electrolyte interface reactivity was made at regular intervals.

2.8. Polarization measurements

Point by point voltage excursions around the rest electrode potential were effected using a Kepco precision voltage source, and the currents were monitored with a 6753 Cimron digital voltmeter and a precision resistor. After each new voltage setting, the current fell to a constant value after a few minutes, and these I–V points defined the micropolarization curves. Anodic and cathodic macropolarization runs (quasi-stationary linear sweeps)

were made using a 557 Amel potentiostat–galvanostat and the corresponding current–potential curves were plotted on a PM8141 Philips XY recorder.

Anodic galvanostatic curves at various current densities were measured to estimate the lithium discharge capability. The electrode potential, as a function of time, was recorded on a 27000 Bryans Xt recorder. Polarization of the electrode was terminated when the potential showed a sudden increase; assumed to be the onset of gross mass-transport effects.

The same equipment, cell, and electrodes employed for the above measurements, was also used for cyclic voltammetry (non-stationary cyclic sweeps) at a potential scanning rate of 20 mV/s.

3. Results and discussion

3.1. Electrolyte conductivities

Examination of our electrolyte system showed that the TBAPr salt is highly soluble and dissociates easily in propylene carbonate; even 1M solutions are far from being saturated. The conductivity–composition plot (Fig. 1) shows an intermediate solution having high conductivity, as indicated by the maximum (5.1×10^{-3} ohm^{-1} cm^{-1}), at 0.6M TBAPr. This value is similar to that observed for solutions of TBACl in the same solvent [8]. Moreover, it is attained at a slightly greater dilution than that required for the chloride solutions (0.65M). Solutions of 0.1M also exhibited adequate conductivities and were used throughout the experimental programme.
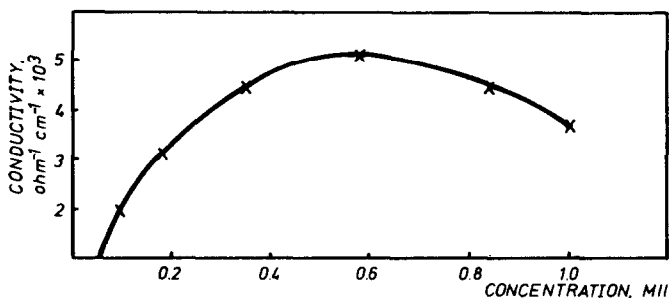

Fig. 1. Specific conductance of propylene carbonate at various TBAPr concentrations.

3.2. Solubility and compatibility results

Following the procedure reported above, we found that the solubility of LiPr in TBAPr(0.1M)–PC was 8.7×10^{-4}M, a value which should ensure a satisfactory shelf-life for batteries using Li/LiPr, Pr^- negative electrodes. As far as the electrolyte reactivity is concerned, our visual examinations did not reveal any particular reaction at the Li/electrolyte interface and the Li surface remained untarnished even on long exposure to the electrolyte. It thus appears that Li is unable to reduce the electrolyte, although the reaction is thermodynamically feasible, as discussed below.

3.3. Mercury–mercurous propionate electrode workability

Of the electrodes of the general type Hg/Hg_2X_2, X^-, the mercury–mercurous acetate electrode in propylene carbonate was reported by Caiola *et al.* [9]. The system was a reference electrode for their work on organic electrolyte batteries. The similarity between the physical properties of mercurous propionate and mercurous acetate suggested that an Hg/Hg_2Pr_2, Pr^- electrode would work satisfactorily in our electrolyte solutions. To test this hypothesis, measurements of the reversibility, the polarizability, the reproducibility and the stability of a propionate electrode were made. Other reference electrodes had been considered, *e.g.*, the calomel electrode [12], and although mercury–mercurous propionate was chosen for the present study, the use of alternatives in future work is not totally ruled out.

If we assume that the electrode behaves in a somewhat similar way to conventional secondary electrodes, then two equilibria will be satisfied in the Hg_2Pr_2 half-cell. Mercurous propionate is soluble to a small extent and is in equilibrium with its ions in the electrolyte

$$Hg_2Pr_2 \rightleftarrows Hg_2^{2+} + 2Pr^-$$
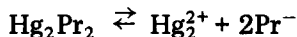
and, at the same time mercury metal is in equilibrium with mercurous ions

$$Hg_2^{2+} + 2e^- \rightleftarrows 2Hg$$
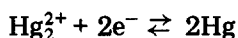
the overall equilibrium being expressed as

$$Hg_2Pr_2 + 2e^- \rightleftarrows 2Hg + 2Pr^-.$$
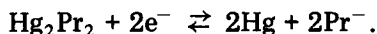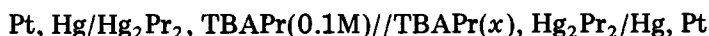
The half-cell reduction potential for this equilibrium can be written

$$E = E^\circ - 0.0591 \log a_{Pr^-}$$

assuming that the temperature is taken as 298.15 K and the activities of Hg and Hg_2Pr_2 are unity.

To verify this equation, the e.m.f. of the cell

$$Pt, Hg/Hg_2Pr_2, TBAPr(0.1M)//TBAPr(x), Hg_2Pr_2/Hg, Pt$$

in propylene carbonate was measured at concentrations (x) varying between 0.01 and 0.1M/l.

The measured e.m.f. values shown in Fig. 2 could not be made to agree with theoretical values obtained from a simplified model and an improved understanding of our electrochemical system will, it is hoped, follow.

To define the system further, the reversible behaviour of the Hg/Hg_2Pr_2 electrode was examined by studying its micropolarization behaviour (Fig. 3). Over the potential range ±40 mV the electrodes can be seen to be reversible and a calculation of the polarization resistance in the system gives a value of 2×10^3 ohm cm^2.

Potential decay tests indicated that the Hg/Hg_2Pr_2 electrodes were easily depolarized.

Comparison of the potentials of two or more, nominally identical, Hg/Hg_2Pr_2 electrodes in the same electrolyte for periods of several days,

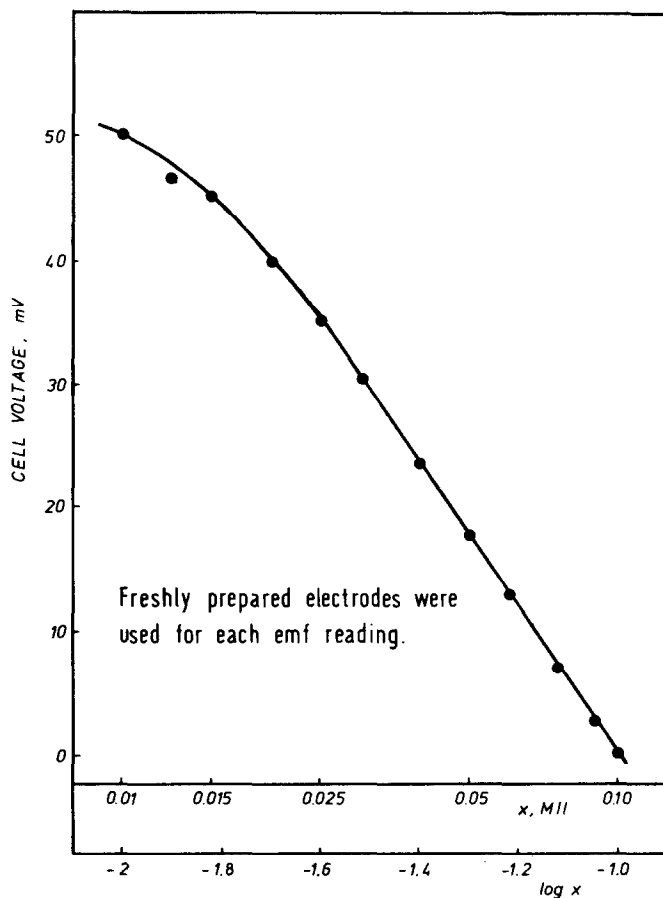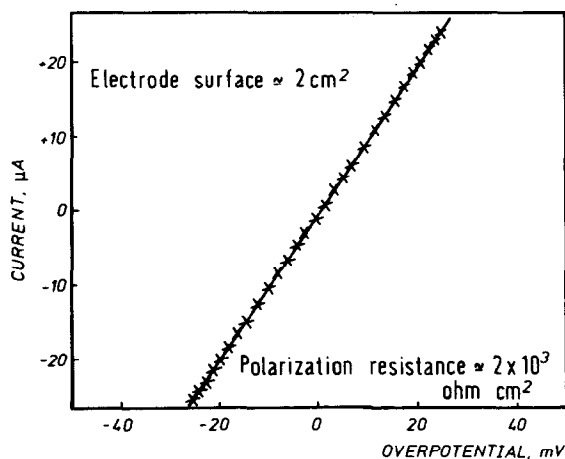Fig. 2. E.m.f. values for the Hg/Hg$_2$Pr$_2$ concentration cell.

Fig. 3. Micropolarization of an Hg/Hg$_2$Pr$_2$ electrode in PC + TBAPr (0.1M/l).

however, led to poor results. The initial potential difference between two electrodes was below 5 mV and remained constant within ±1 mV for about 6 h but then it increased to 10 - 20 mV, increasing with the ageing of the electrodes. At the same time, slow dissolution of the Hg_2Pr_2 occurred with the formation of a yellow–green layer (possibly a mercuric propionate complex) and, after 5 - 6 days, only a dark grey, finely-divided substance on the mercury surface could be observed. Microscopic examination showed that this consisted mainly of mercury globules. The unsatisfactory ageing behaviour of the reference electrode may thus be attributed to the disproportionation of the mercurous propionate in a similar way to that observed by Caiola et al. [9, 10] for the electrode Hg/Hg_2Ac_2 and Hg/Hg_2SO_4 in propylene carbonate and dimethyl sulphate, and by Baucke and Tobias [13] for the electrode Hg/Hg_2Cl_2 in propylene carbonate.

Due to the electrode disproportionation all the potentials described below are measured with respect to a freshly prepared Hg/Hg_2Pr_2, Pr^- (0.1M) reference electrode.

3.4. Lithium electrode behaviour

Figure 4 shows the results of a micropolarization experiment on a lithium electrode. The cathodic and anodic plots form a continuous straight line with no appreciable hysteresis, suggesting that the electrode can be operated reversibly. An exchange current density of 0.01 mA/cm² was calculated from the slope of the line and from the area of the electrode. It is realised that the accuracy and validity of these results may be brought into question on the grounds that the reference electrode is not stable. This, however, is not the case; it has been shown that the Hg/Hg_2Pr_2, Pr^- system can be considered as a "true reference electrode" if it is used immediately after being prepared, and all results reported here were obtained under such conditions.
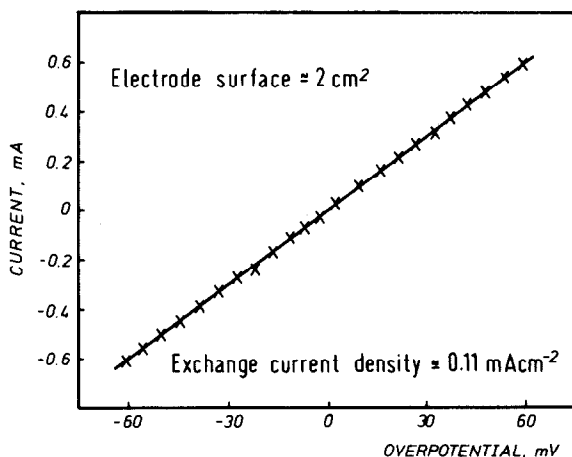

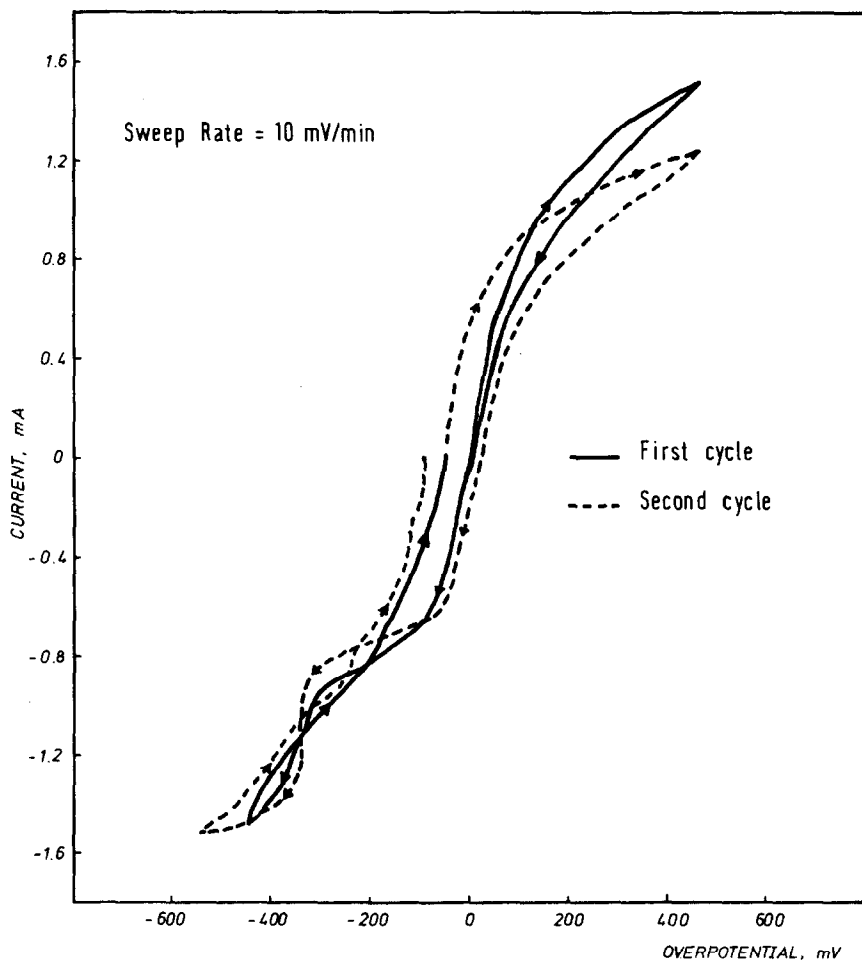Fig. 4. Lithium micropolarization in PC + TBAPr (0.1M/l).

Fig. 5. Lithium macropolarization in PC + TBAPr (0.1M/l).

Further investigation by the macropolarization technique indicated that good reversible behaviour of the lithium electrode is only obtained within a narrow overpotential range (about ±60 mV). This is shown by the macropolarization behaviour of the lithium electrode reported in Fig. 5. The observed relaxation effect (shown by the anodic curves) may be due to mass transport effects related to the LiPr precipitation, effects which would be more pronounced as cycling and overpotential is increased. LiPr was clearly revealed after an anodic polarization of the electrode surface at a constant potential of −2900 mV for some hours.

Cyclic voltammetry measurements also confirmed the lithium electrode behaviour (Fig. 6). After completion of the 9th cycle, a cathodic polarization of 300 - 500 mV overpotential was applied to the electrode for 1 - 2 h, the behaviour of Li during the subsequent cycle remained identical to that
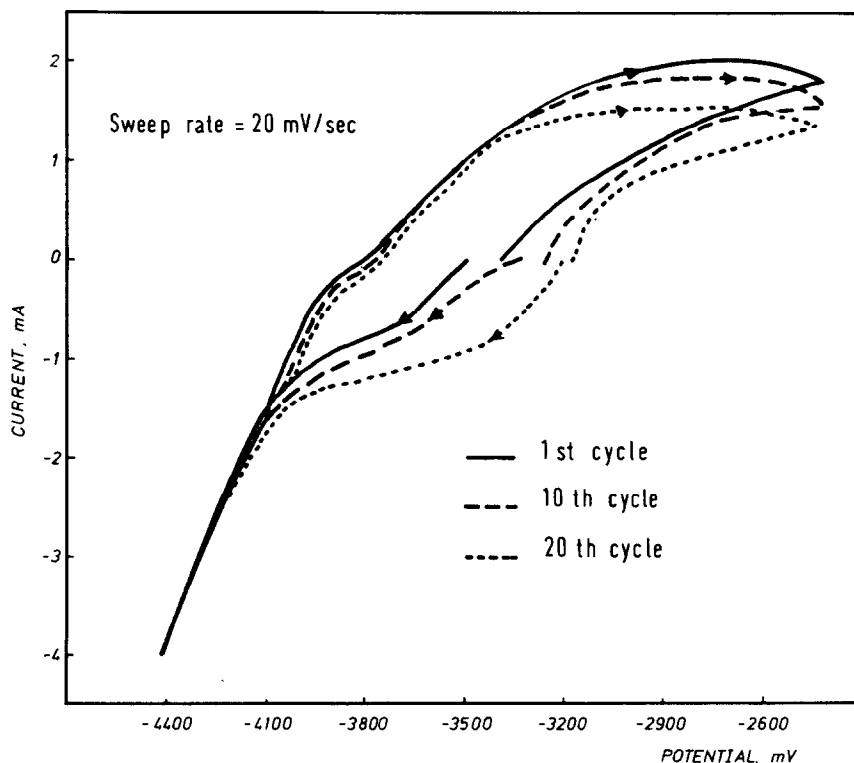
Fig. 6. Lithium cyclic voltammograms in PC + TBAPr (0.1M/l).

shown by the first cycle, *i.e.*, a cathodic prepolarization is able to reduce the LiPr and clean the electrode surface.

To determine the current densities below which cycling could be carried out without major deterioration of the electrochemical properties of the lithium electrode, studies were conducted in the galvanostatic mode. As is shown in Fig. 7, at 0.25 mA/cm^2, the overpotential is about 80 mV and remains constant for many hours. At 0.5 mA/cm^2, the overpotential is about 180 mV, gradually increasing with time. The curve is similar at 0.75 mA/cm^2 but a sudden increase of overpotential, revealing development of large concentration polarization, occurs after 5 h.

Polarization enhancement begins after 3 h at 1 mA/cm^2 and at 1.25 mA/cm^2 we observed a rapid tendency towards higher anodic potentials. Therefore, only at current densities lower than 0.25 mA/cm^2 can it be ensured that the 60 mV threshold overpotential value, which limits the reversible electrode behaviour region, will not be exceeded except during a short transient period ($\sim$15 min).

3.5. Electrolyte reduction

The solubility and compatibility tests performed during this study suggested that the lithium/electrolyte reactivity is pratically nil. No colour
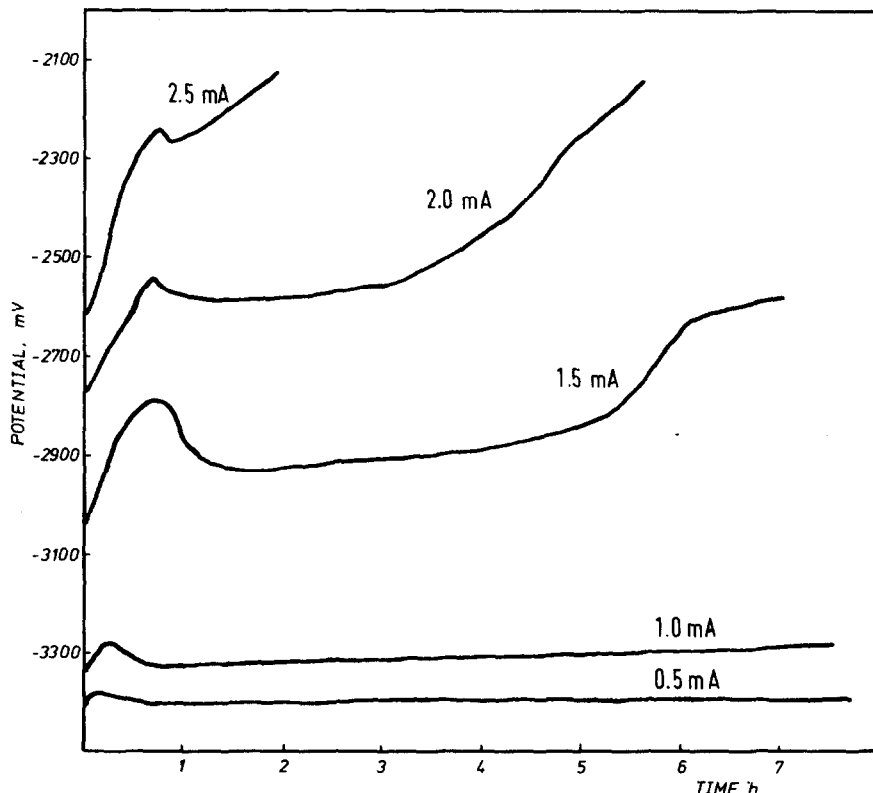
Fig. 7. Galvanostatic behaviour of lithium in PC + TBAPr (0.1M/1).

change in the electrolyte, no blackening of the electrode and lack of gas evolution all indicate that no chemical degradation occurred during the course of the tests. As pointed out by Selim and Bro [14], however, any polar solvent is intrinsically reactive toward lithium because of the existence of an electron deficient region about a highly electronegative atom, which forms the positive end of the dipole. This intrinsic reactivity may go undetected by the static tests reported here but may be crucial in cycling experiments, particularly after appreciable periods of time.

The decomposition of propylene carbonate accompanied by the formation of propylene gas according to the reaction

$$CO_3C_3H_6 + 2Li \rightarrow Li_2CO_3\downarrow + C_3H_6\uparrow$$
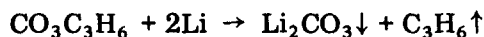
was observed by Dey [15]. The thermodynamic instability of PC in the presence of Li was thus established. Kedrinskii and co-workers [16] have also shown that all aprotic organic solvents suitable for Li battery electrolytes are thermodynamically unstable with Li.

To determine whether such chemical instability persists or not in the Li/TBAPr + PC system we determined the cathodic limits of the electrolyte.
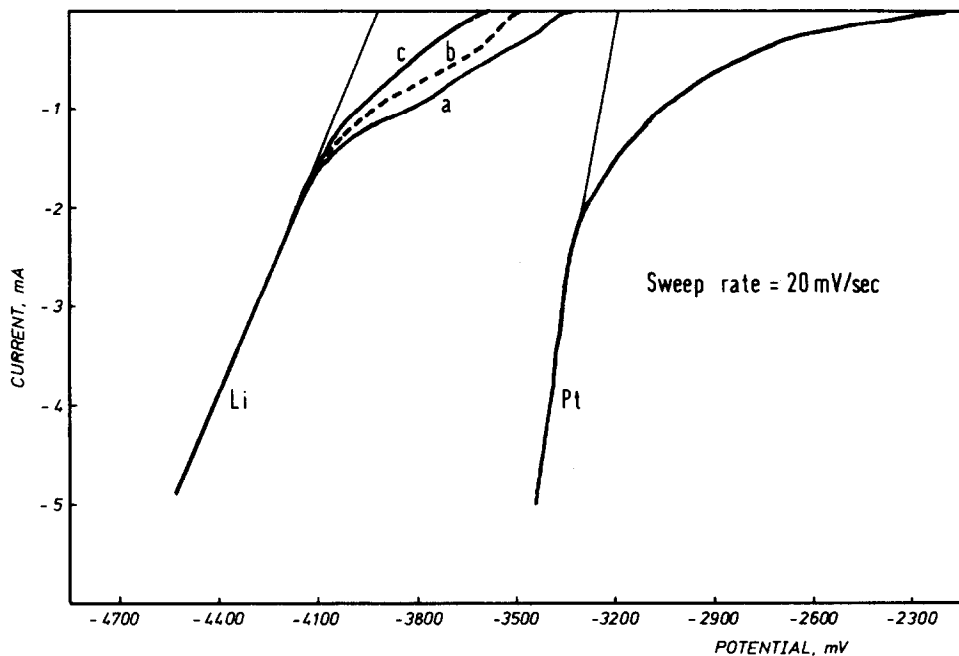
Fig. 8. Reduction of PC + TBAPr (0.1M/l) on Li and Pt electrodes.

Therefore, after the usual loading procedures, classical cathodic voltam-
mograms were recorded on Pt and Li electrodes and are shown in Fig. 8. The
cathodic limit on Pt (—3.2 V) occurs at a potential 0.3 V more positive than
the Li rest potential (—3.5 V) (curve (b)). At this potential the electrolyte
reduction on Pt occurs with a significant discharge rate (>2.5 mA/cm^2). On
the other hand, the cathodic limit on Li occurs at a potential 0.72 V more
negative than on Pt (—3.92 V). This high overpotential for the electrolyte
reduction on Li allows reductions of the lithium salt to the metallic state
prior to the solvent reduction.

Figure 8 also shows the reduction curves for a Li electrode anodically
prepolarized at —2.9 V for 2 h (curve (a)) and for a Li electrode which was
immersed in the solution and immediately "cleaned" at a cathodic potential
of —3.8 V for 30 min prior to obtaining the reduction curve (curve (c)). The
differences between curves (a), (b), and (c) are due to the LiPr formation on
the Li surface, the potential range available for its reduction being of the
order of 0.4 V.

4. Conclusions

In this work a new lithium electrode has been described and prelimi-
nary data on its electrochemistry presented. The electrode is reversible pro-

vided that the overpotential does not exceed 60 mV. Beyond this value, the anodic curve shows a relaxation effect due to mass-transport phenomena. These phenomena may play an important role by retarding the Li/electrolyte reaction kinetics, whose thermodynamic instability has been determined.

The galvanostatic curves revealed that Li may be able to deliver current densities of the order of 0.25 mA/cm^2 for several hours without appreciable polarization.

For these studies a mercurous propionate electrode was assembled and its usefulness as a "reference electrode" was observed when using freshly prepared electrodes.

Acknowledgement

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