DISCHARGE CHARACTERISTICS AND INTERFACE IMPEDANCE OF AN Li/1 M LiClO$_4$(PC)/V$_2$O$_5$ CELL

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Summary

A laboratory-type lithium cell has been assembled with a pure V$_2$O$_5$ cathode and a non-aqueous electrolyte consisting of LiClO$_4$ dissolved in propylene carbonate. Cell discharge characteristics have been studied under different resistive loads. The interface reaction of the cell has been followed by complex-plane impedance analysis. Both the anodic and cathodic interfaces contribute significantly to the electrode polarization. While the anodic interface is characterized by the formation of a passive film on the lithium surface, the cathodic process is dominated by lithium diffusion into the V$_2$O$_5$ lattice. An Mn-doped V$_2$O$_5$ cathode is found to react chemically with the electrolyte, thereby increasing its resistance.

Introduction

The present interest in high energy-density batteries based on metallic lithium as the anode has generated much research into the development of suitable electrolytes (either solid or liquid), and also into cathode materials — particularly of the intercalation compound type. In addition to having a high energy density, lithium cells are also characterized by having high open-circuit voltage and long shelf-life. While the search for a good lithium-conducting solid electrolyte still continues, several non-aqueous liquid electrolyte systems have been found to be very promising and some of them are being exploited commercially.

Cyclic esters, such as propylene carbonate (PC), are found to dissolve a variety of lithium salts (*e.g.*, LiClO$_4$, LiAsF$_6$, LiBF$_4$, etc.) and to provide a reasonably good lithium-conducting electrolyte. In spite of the thermodynamic instability of metallic lithium in contact with these non-aqueous electrolytes, the metal is found in practice to be stable. This is due to the formation of a protective film that is possibly lithium carbonate [1].

Many soluble (*e.g.*, liquid SO$_2$, SOCl$_2$) and insoluble materials (*e.g.*, various oxides of vanadium, CuS, Ag$_2$CrO$_4$, CF$_x$, etc.) have been examined as the cathode for these batteries. In recent years, there has been a renewed

interest in the use of various transition metal sulphides and oxides as cathode materials, mainly because of their high electronic conductivity and very good rechargeability. These compounds — either because of their van der Waals bonded, two-dimensional layered structure; or three-dimensional framework, tunnel structure — undergo topotactic reactions with lithium. These lead to intercalation of lithium into the cathode structure. Some of these compounds so far investigated include: TiS_2 [2 - 4]; MoO_3 [5]; Nb_2O_5 [6]; V_2O_5 [6, 8]; and V_6O_{13} [8, 9].

In this investigation, we have examined the discharge characteristics of a lithium cell that used a non-aqueous electrolyte ($LiClO_4$ dissolved in propylene carbonate) and a V_2O_5 cathode. The interface reaction was characterized by complex impedance analysis. The effect of Mn-doping of the V_2O_5 cathode was also studied.

Experimental

Vanadium pentoxide in the form of a compact disc was made by sintering cold-pressed pellets at 600 °C in an argon atmosphere for 24 h. Mn(IV)-doped V_2O_5 was prepared by conventional solid-state sintering. In the procedure, weighed amounts of MnO_2 and V_2O_5 were mixed thoroughly and the mixture was then pressed and sintered in the same manner as for pure V_2O_5.

The cell was assembled in a Teflon holder and is shown schematically in Fig. 1. Two stainless-steel discs were used as the current collectors. Mechanically cleaned, lithium metal foil (Alfa Chemicals, U.S.A.) of thickness about 0.38 mm was used as the anode. The electrolyte solution was prepared by dissolving anhydrous $LiClO_4$ (Alfa Chemicals, U.S.A.) in propylene carbonate (Koch-Light Lab., U.K.). The latter two chemicals
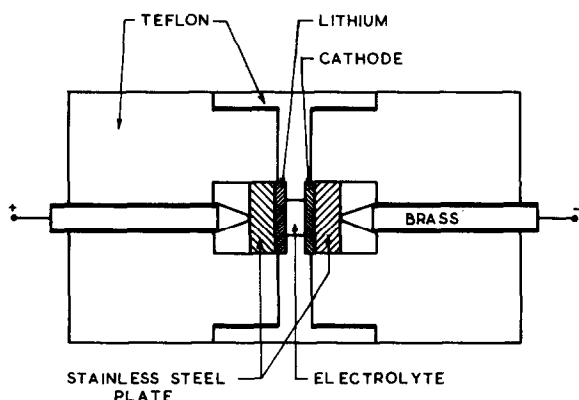

Fig. 1. Sample holder for electrochemical measurements.

were carefully dehydrated before use: the PC by vacuum distillation
followed by passing through a Linde 5 Å molecular sieve, and the $LiClO_4$
by vacuum drying at 300 °C for 8 h. The electrolyte was soaked in a com-
pressed cotton pellet (~3 mm thick) which was then sandwiched between
the lithium foil and the V_2O_5 cathode pellet (2 - 3 mm thick). The
diameter of all the pellets was about 10 mm. The cell was both assembled
and tested inside an argon-filled glove box having below 10 p.p.m. of
moisture.

During discharge, the cell was connected to various resistive loads and
both the voltage and the current were measured as a function of time. The
cell voltage was recorded using a Keithley 616 digital electrometer and the
current using a digital multimeter. The capacity of the cell was calculated
by measuring the area under the current/time plots. The complex impedance
of the cell was determined at different frequencies after different periods
of discharge. Measurements of impedance were carried out between 5 Hz
and 13 MHz using an HP impedance analyser (Model LF 4192A).

Results and discussion

The discharge characteristics of the cell using a pure V_2O_5 cathode
under different loads are shown in Fig. 2. As expected, the cell voltage
remains constant over a long period when the load is comparatively high
(33 kΩ) and, correspondingly, the current is low (~90 µA). However, as the
load is decreased, the current increases and the cell voltage drops quite
sharply. At low loads, the current also drops quite significantly within a very
short time (see, for example, Fig. 3). We point out here that the capacity
of our cell is some orders of magnitude lower than that of prototype
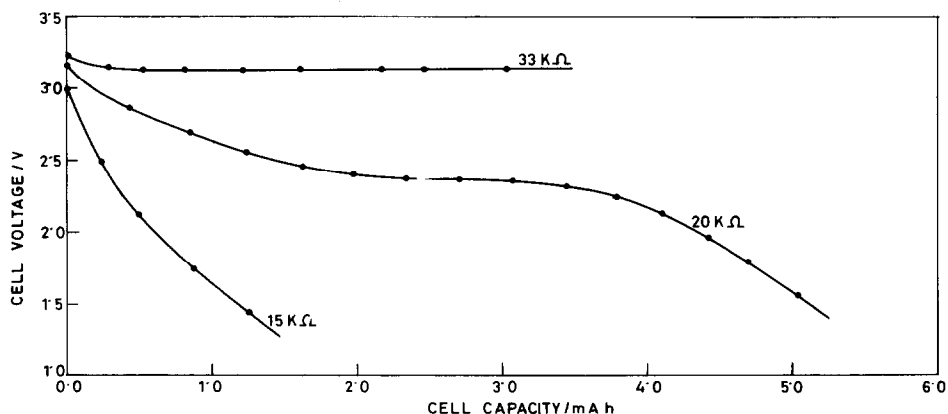batteries manufactured by certain commercial agencies [10, 11]; this is

Fig. 2. Discharge curve at room temperature of an Li/1 M $LiClO_4(PC)/V_2O_5$ cell with
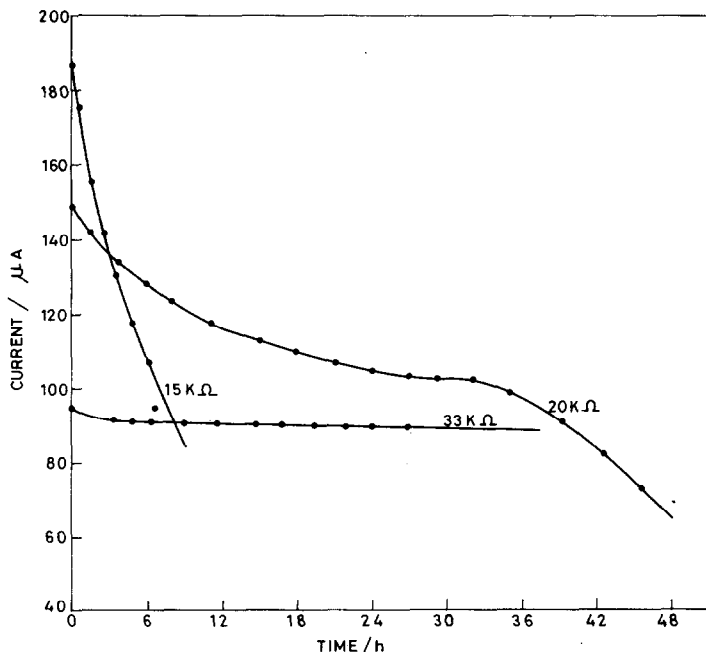different loads.

Fig. 3. Current *vs.* time plot of an Li/1 M LiClO$_4$(PC)/V$_2$O$_5$ cell under different loads.

mainly because of the greater thickness of both the electrode and the electrolyte and also because of the less efficient current-collecting system used in our cell construction. However, the present cell design was adequate to serve the main purpose of this investigation, namely, the study of the electrode/electrolyte interface reactions. The open-circuit voltage of the cell was found to be around 3.5 V; this compares favourably with reported values [1, 10].

The discharge process was also followed by the measurement of a.c. impedance of the cell at different intervals. Figure 4 shows the resulting impedance diagrams in which the imaginary part of the complex impedance is plotted against the real part as a function of the frequency. At each stage of the discharge process, the impedance diagrams exhibit two arcs at different frequency ranges. The high frequency arc passes through the origin and is nearly semicircular while the low frequency arc is significantly depressed (about a quarter of a circle). During discharge, the shape and size of the high frequency arc remain unaltered but the low frequency arc exhibits a decrease in size (see Figs. 4(b) and (c)). The incompleteness of the low frequency arc in Fig. 4(a) is due to the limitation of the measuring equipment. From impedance analysis theory, one can safely assume that the high frequency semicircular arc in Fig. 4 corresponds to ionic transport in the bulk of the electrolyte and in the electrodes. As expected, this characteristic does not change throughout the discharge process. On the other
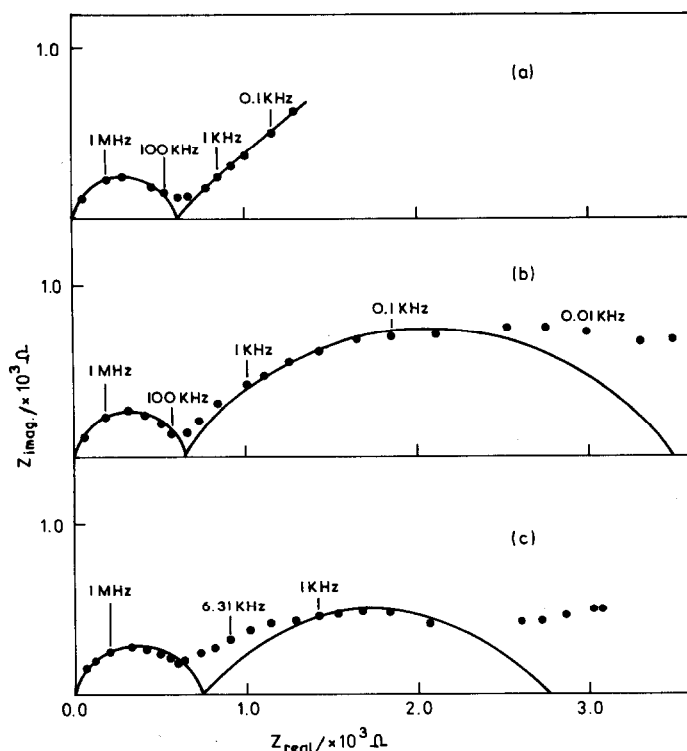
Fig. 4. Impedance diagram of an Li/1 M LiClO₄(PC)/V₂O₅ cell after different times of discharge: (a) no discharge; (b) 25 h; and (c) 80 h.

hand, the low frequency arc reflects phenomena occurring at both the anode/ and cathode/electrolyte interfaces, and the interfacial characteristics change during the discharge. Although exact quantitative analysis of this change is difficult to achieve from the data available, certain qualitative conclusions may be drawn. The total interface resistance is approximately represented by the real-axis intercept of the low frequency arc, and is seen to decrease with time. This is contrary to the expected increase in interface resistance due to polarization effects. The quarter-circle representation of the impedance diagram is an indication of a diffusion-controlled reaction, rather than a simple charge-transfer process, and this characteristic continues throughout the discharge cycle. Considering these effects, it can be concluded that the interfacial process is dominated by the diffusion of lithium ions through a lithium-rich intercalated layer that is formed on the cathode surface and grows in thickness as the discharge proceeds. Note that the resistivity of V_2O_5 decreases as more lithium is intercalated into its structure, particularly at lower concentrations of lithium [12], and this is probably the cause of the decrease in the interface resistance.

In order to study the anode/ and cathode/electrolyte interface reactions separately, impedance measurements were also carried out on two symmetric cells with either metallic lithium or pure V_2O_5 as the two electrodes. Figure 5 shows the impedance diagrams for the all-lithium cell measured after increasing lengths of time from assembly (open-circuit). Interestingly,
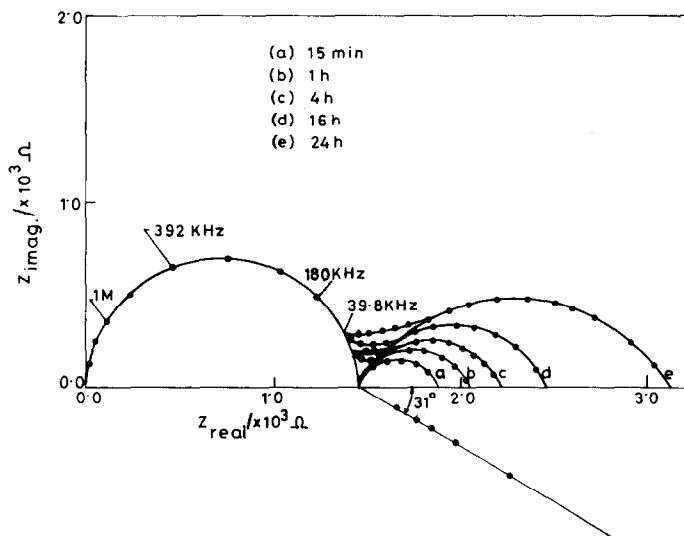

Fig. 5. Impedance diagram of an Li/1 M LiClO$_4$(PC)/Li cell at different times after assembly.

the high frequency semicircle (corresponding to the electrolyte process) does not change with time, but the interfacial semicircle grows systematically. This is indicative of a systematic increase in the interface resistance. The presence of this second arc suggests that the metallic lithium is kinetically irreversible to the liquid electrolyte. Since there is no possibility of electrochemical lithium transport in this experiment, the increase of interface resistance is clearly due to the formation of a passive film on the lithium metal surface in contact with the electrolyte. The thickness of this film increases with time. The fact that the low frequency arc is dominated by the lithium transport across the film may be confirmed by the following two observations: (i) the equivalent resistance R_F of the process (measured from the real-axis intercept of the low frequency arc) increases with time in accordance with the increase of film thickness; and (ii) the equivalent capacitance C_F decreases with time. The changes in these two quantities with time are given in Table 1. The change in R_F provides information on the kinetics of the film growth. It is observed that R_F follows a straight-line relationship with the square root of time (Fig. 6) and thus suggests a parabolic law for the growth kinetics. The formation of such a film is a proven phenomenon for lithium batteries using non-aqueous electrolytes [1, 13,

TABLE 1

Variation of resistance and capacitance of anodic film with time

Time (min)	15	60	240	600	1440
Resistance (Ω)	420	600	740	1000	1680
Capacitance (10^{-7} F)	3.80	2.65	2.15	1.59	1.50

14]. However, the present results indicate that this reaction between the metal and the electrolyte does not in any way change the characteristics of the electrolyte, it only affects the interfacial process whose equivalent resistance may be as high as that of the electrolyte and is possibly the principal source of electrode polarization. It may also be noted in Fig. 5 that, compared to the nearly perfect semicircular arc at high frequencies, all the low frequency arcs are greatly depressed (by nearly 30°). This may indicate the formation of a film with a disordered structure.
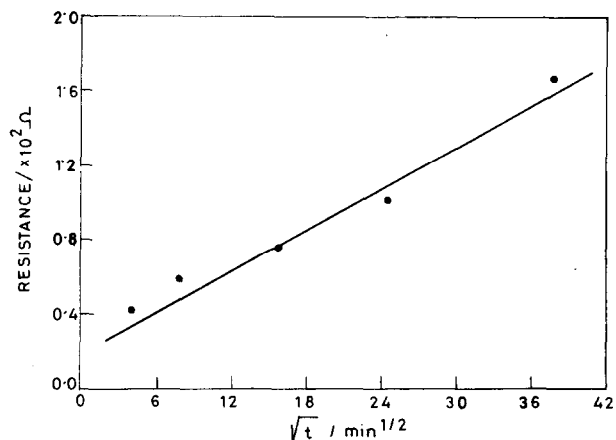

Fig. 6. Time dependence of film resistance on the lithium electrode.

The impedance diagram of a symmetrical V_2O_5 cell is shown in Fig. 7 and is seen to consist of three, closely spaced, circular arcs. Interestingly enough, this diagram does not change with time, suggesting that there is no chemical reaction between the electrolyte and the electrode as was the case in the lithium cell. As before, the highest frequency semicircle arises from relaxation of the bulk electrolyte. The intermediate arc possibly results from the charge-transfer reaction at the interface. The lowest frequency arc corresponds to the process of lithium diffusion into the V_2O_5 lattice. The presence of the low frequency arcs indicates that V_2O_5 is also not a kinetically reversible electrode for this electrolyte and plays a significant role in the electrode polarization. Considering the equivalent circuit for this system to be a series combination of R–C lumped circuits, one can
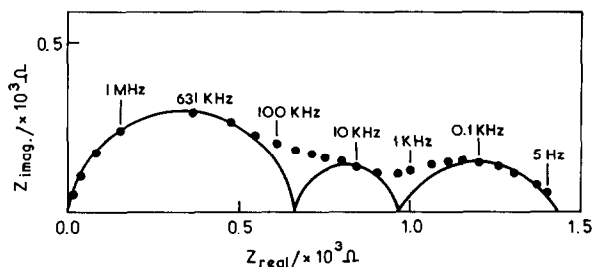
Fig. 7. Impedance diagram for a $V_2O_5/1$ M $LiClO_4(PC)/V_2O_5$ cell.

determine both the bulk electrolyte resistance R_b and its geometric capacitance C_g, the charge-transfer resistance R_c, and the double-layer capacitance C_d. The values of these parameters, calculated from the impedance diagram, are given in Table 2.

TABLE 2

Equivalent circuit parameters for a $V_2O_5/electrolyte/V_2O_5$ cell

R_b	C_g	R_c	C_d
660 Ω	3.82×10^{-10} F	300 Ω	5.31×10^{-8} F

It is known that pure V_2O_5 is not a very good electronic conductor. Thus, a possible means of reducing electrode polarization in an Li/1 M $LiClO_4(PC)/V_2O_5$ cell may be to use a more conducting cathode such as Mn-doped V_2O_5. The latter material has been found to have a higher electronic conductivity than pure V_2O_5, namely, $\sim 10^{-4}$ Ω^{-1} cm^{-1} (Fig. 8). In an attempt to improve cell performance, the discharge characteristics of an Li/1 M $LiClO_4(PC)/(Mn_{0.03}V_{0.97})_2O_5$ cell were studied; the results are given in Fig. 9. Surprisingly, the performance was not found to improve:

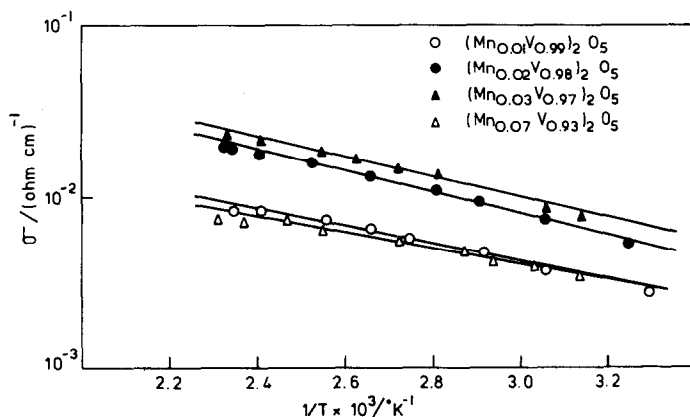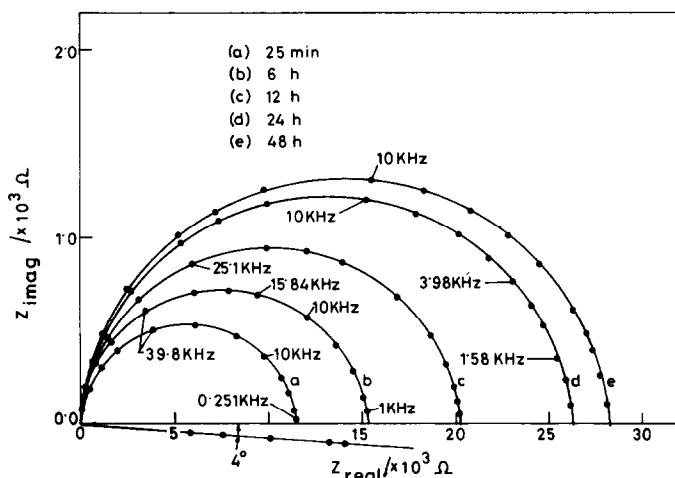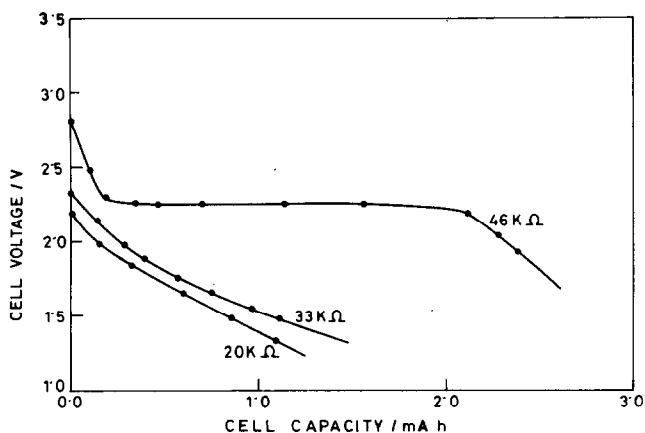Fig. 8. Conductivity of V_2O_5 doped with Mn(IV).

Fig. 9. Discharge curve at room temperature of an Li/1 M LiClO$_4$(PC)/(Mn$_{0.03}$V$_{0.97}$)$_2$O$_5$ cell with different loads.

Fig. 10. Impedance diagram for an (Mn$_{0.05}$V$_{0.95}$)$_2$O$_5$/1 M LiClO$_4$(PC)/Mn$_{0.05}$V$_{0.95}$)$_2$O$_5$ cell at different times after assembly.

more severe polarization was observed. A plateau in the discharge curve was obtained when the load was more than 46 kΩ. There was also a considerable drop in the cell voltage. We attribute the latter to a chemical reaction between the Mn-doped cathode and the electrolyte. As is not the case with lithium metal, the reaction results in an increased electrolyte resistance. This is clearly demonstrated by the variation with time of the impedance diagram obtained for a cell having Mn-doped V$_2$O$_5$ electrodes placed symmetrically on either side of the electrolyte (Fig. 10). The electrolyte resistance increases with increasing contact time. The exact nature of the reaction is not clear at this stage and a further, more detailed, investigation is planned.

Conclusions

As a result of this study on Li/LiClO$_4$(PC)/V$_2$O$_5$ cells, we draw the following conclusions.

(i) Both the lithium anode and the V$_2$O$_5$ cathode are kinetically irreversible to the LiClO$_4$(PC) electrolyte. Film formation on the lithium surface and diffusion of lithium into the V$_2$O$_5$ lattice are the predominating mechanisms of electrode polarization.

(ii) The chemical reaction between the anode and the electrolyte does not change the bulk characteristics of the electrolyte.

(iii) The kinetics of the film growth follow a parabolic law.

(iv) Mn-doped V$_2$O$_5$ has a higher conductivity than pure V$_2$O$_5$, but is not a suitable cathode for the above cells; the doped material reacts with the electrolyte and increases its specific resistance.

Acknowledgement

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