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Passivation of porous carbon cathodes in lithium–thionyl chloride cells

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The passivation of porous carbon cathodes in 1.8 M $LiAlCl_4$–$SOCl_2$ solution has been studied. The electrodes were galvanostatically discharged for a range of current densities and electrode thicknesses. The results show that the passivation of the cathode is controlled by the rate of diffusion of the LiCl product away from the electrode. This was shown by the ability of passivated glassy carbon to recover capacity for $SOCl_2$ reduction when allowed to stand in the electrolyte solution.

The results show that there is a limiting cathode thickness beyond which additional carbon loading fails to increase the passivation time.

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1. Introduction

The lithium–thionyl chloride primary cell has one of the highest energy densities in existence. The low equivalent weight and long shelf life have also led to much interest in the cell [1]. It consists of a lithium foil anode isolated from a porous carbon cathode by a ceramic separator.

The overall cell reaction may be simply expressed as:

$$4Li + SOCl_2 \longrightarrow 4LiCl + SO_2 + S$$

The mechanism is more complex, however, with various intermediates having been proposed [2–5].

It is widely accepted that the porous carbon cathode becomes progressively blocked by a deposit of LiCl and this is the major reason for cell failure [6]. Addition of electrocatalysts to the cathode have been shown to increase cell capacity, the best known being platinum [7], copper halides [8] and various metal phthalocyanines [9].

For this work it was considered of interest to engage upon a more fundamental study of the carbon cathode. Specifically, interest centred on the time taken to passivate various thicknesses of uncatalysed carbon cathodes. For these experiments it was possible to prepare a range of cathodes including very thin ones ($\sim 1\,mg\,cm^{-2}$). In addition smooth, glassy carbon was included for comparison purposes.

Similar work has actually been undertaken by Hagan *et al.* [10] in which the transition times of porous carbon electrodes for different concentrations of $LiAlCl_4$ dissolved in the $SOCl_2$ were studied. This technique has been used for the study of smooth [11, 12] and porous zinc anodes in potassium hydroxide solutions. The results of the latter study showed that an insoluble deposit was formed within the porous matrix, in a similar manner to the LiCl on porous carbon.

Passivation usually results in an abrupt change in potential due to the surface concentration of the electroactive species reducing to zero at the electrode interface. For the carbon cathode in the Li–$SOCl_2$ cell this is due to the presence of LiCl, which is a poor conductor, on the electrode surface, eventually preventing further reduction of thionyl chloride, i.e. the electrode is blocked.

In the absence of convection, Sand [13] developed an equation governing transition

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time:

$$(1/\tau^{1/2}) = 2i/ZF(\pi D)^{1/2}A|C - C_{\text{crit}}| \qquad (1)$$

where, τ is the time for the concentration of products at the electrode surface to change to a value necessary to cause passivation, i is the current density, z is the valency charge, C is the concentration of products in the bulk electrolyte, and C_{crit} is that concentration at the electrode necessary to bring about passivation, D is the diffusion coefficient of electroactive species, F is the Faraday constant, and A is the electrode area.

The results for such a diffusion-controlled reaction imply that a plot of $\tau^{-1/2}$ versus i should be a straight line with a gradient given by

$$\partial\tau^{-1/2}/\partial i = 2/zF(\pi D)^{1/2}A\Delta C \qquad (2)$$

This relationship, although originally derived for smooth electrodes in aqueous solution, has been found to hold for porous carbon in thionyl chloride at higher current densities. (It is interesting to note that at these high rates the reaction is thought to be largely rate-controlled by diffusion).

It was the aim of this study to explore the relationship between passivation time (active reaction time) and other variables of interest to technologists, and generally optimize the behaviour of the system.

2. Experimental details

For this study the cathodes were prepared by spraying a mixture of carbon (Shawinigan Acetylene Black) and PTFE (10% w/w, ICI plastics) onto a nickel stud (area = $2.54\,\text{cm}^2$). The carbon–PTFE mix was fully homogenized with 1,1,1-trichlorethane before spraying. After drying in an oven at 100° C, layers of carbon were removed from the surface of the stud, using a microtome, until the required thickness of cathode was obtained. It was found that $\sim 1.97\,\text{mg}\,\text{cm}^{-2}$ of carbon corresponded to a thickness of $100\,\mu\text{m}$. Using such a finely dispersed carbon deposit it was possible to administer accurately small quantities of carbon onto the stud. It is recognized that all the cathode thicknesses quoted in this work are for electrodes prepared by the above method and are likely to be reduced as the cathodes are compressed in the cell.

The lithium anodes were prepared by pressing a piece of lithium foil (99.9%, Lithco. Ltd) onto a nickel mesh current-collector (Expamet Co. minimesh). The anode had an area of $3.24\,\text{cm}^2$.

The electrolytic cell was constructed from PTFE and provided accommodation for the nickel stud and mesh. A piece of ceramic separator paper was placed between the electrodes. Arrangement within the cell was made for a lithium foil reference electrode (area = $0.1\,\text{cm}^2$) next to the cathode. All potentials were measured against this electrode, thus eliminating any possibility of the anode influencing cathode failure.

The electrolyte employed throughout this work was 1.8 M $LiAlCl_4$, made by dissolving stoichiometric quantities of LiCl (Fluka, >98%) and $AlCl_3$ (Fluka, >99%) in $SOCl_2$ (Fisons Ltd, > 98%). A small excess of LiCl was then added to ensure complete neutralization of the electrolyte. Any excess solid remaining was assumed to be LiCl and removed. The whole process of cell assembly took place within an argon-filled dry box (H_2O level < 40 p.p.m.).

Electrical contacts to the cell were made via the nickel stud and nickel mesh. The current source used was a potentiostat (Thompson Electrochem. Ltd), the voltage transients being recorded using a *Y–t* type chart recorder (Curken).

3. Results and discussion

Fig. 1 shows a voltage–time transient for a cathode, $300\,\mu\text{m}$ thick, with $50\,\text{mA}\,\text{cm}^{-2}$ being applied to it. This is typical of all the transients obtained. The curve is characterized by an initial rapid fall in potential from the open circuit voltage as the electrode is polarized, followed by a voltage ramp. As the electrode becomes completely blocked by a passivating layer of LiCl, there is a rapid decrease in potential until the trans-passive region, after which a steady potential is reached.

There is no well-established method of measuring the transition time. This work involved a similar system to that used by Hagan *et al.* [10] and consequently τ was evaluated in a similar way. The two approximately linear portions of

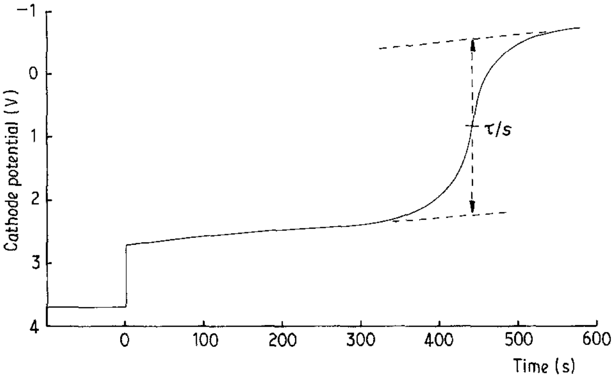

Fig. 1. A typical voltage transient for a cathode, 300 μm thick, at 50 mA cm^{-2}, showing how the transition time is evaluated.

the transient were extrapolated and the point on the rapidly rising portion which bisects the two lines was taken as the transition time. This method was generally found to be very satisfactory since τ could be judged to a precision of ~1% of the reaction time.

Voltage transients for carbon cathodes at various current densities were obtained and analysed. The current density applied to the cathode was found to be inversely proportional to the square root of the transition time. Plots of $\tau^{-1/2}$ versus i for a range of cathode thicknesses are displayed in Fig. 2. As can be seen, a reasonable linear relationship exists for the current densities investigated. It is also apparent that each line in Fig. 2 passes through the origin. This behaviour is characteristic of a diffusion-controlled process in this limited range of current densities.

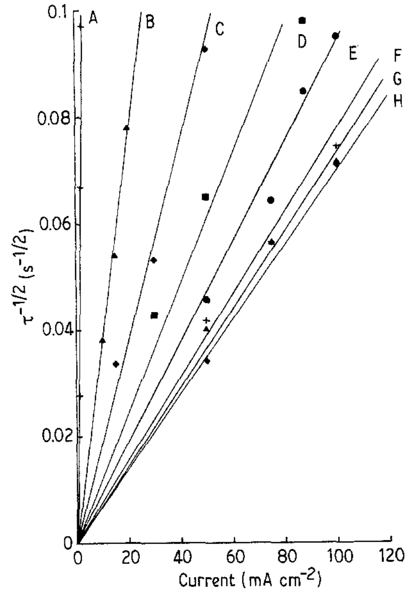

Fig. 2. Plots of $\tau^{-1/2}$ versus i for various thicknesses of carbon cathode. (A) Glassy carbon. (B–H) Porous carbon at the following thicknesses (μm): (B) 50; (C) 100; (D) 200; (E) 300; (F) 400; (G) 500; (H) 600.

Since the final passivating layer on the cathode is LiCl, the reaction is controlled by diffusion of the product away from the electrode. This process continues until the concentration of LiCl at the electrode becomes critical, when the solution capacity for LiCl is exceeded at the electrode and solid LiCl is deposited. This has been confirmed by allowing a glassy carbon electrode to remain on open circuit for 30 min after passivation; on repolarization a similar reaction time was obtained. The open circuit ‘rest’ had enabled the bulk solution to completely remove the LiCl layer. We consider that this arises because the solubility of LiCl in the electrolyte solution exceeds the stoichiometry required by $LiAlCl_4$ [10]. On standing, the solid-phase LiCl at the electrode back dissolves and the cathode depassivates. Dissolved SO_2 from the cathode reaction also complexes with the LiCl produced and thereby increases the solution capacity to remove LiCl.

Using porous electrodes it was found that in an open glass cell, without the presence of separator paper between the electrodes, the thinnest (50 μm) cathodes recovered about one third of their original capacity on resting for 30 min, after passivation at 15 mA cm^{-2}. Thicker cathodes (100 μm), after passivation at 30 mA cm^{-2}, recovered about 20% of their capacity after 30 min rest.

Further examination of Fig. 2 shows that a limit is reached; after thickening the cathode

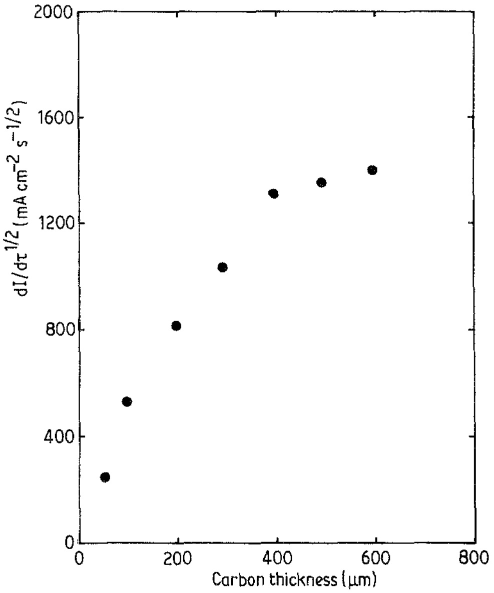

Fig. 3. Graph showing the relationship between (l/slope) of the lines in Fig. 2 and thickness.

beyond ~400 μm little increase in passivation time is observed. This is clearly demonstrated by the slope $\partial\tau^{-1/2}/\partial i$. This relationship is non-linear with thickness, and the thinner deposits behave as intermediates in the progression from a truly planar electrode to one which is 'infinitely porous' in the sense of de Levie [14]. A plot of $(\text{slope})^{-1}(\partial i/\partial\tau^{-1/2})$ (Fig. 3) versus the cathode thickness was found to be approximately linear for the range up to 400 μm; this behaviour is in accordance with the results of Frumkin [15]. Beyond this thickness it was found that there is virtually no increase in passivation time for current densities of 100 mA cm^{-2}. However, the passivation time is still increasing with cathode thickness when current densities of 50 mA cm^{-2} are applied. This accounts for the slight continuing increase in $\partial I/\partial\tau^{-1/2}$ shown in Fig. 3 beyond 400 μm. This can be predicted from the theory of de Levie who showed that the penetration depth of a porous electrode decreases with increasing current density.

The linear portion of Fig. 3 is in accordance with Equation 2, the slope $\partial\tau^{-1/2}/i$ is inversely proportional to A, the effective electrode area, which increases with the thickness. From this relationship it was possible to calculate effective diffusion coefficients, D, for each thickness, based on the apparent surface area of the electrode (see Table 1). The ΔC term in Equation 2 was taken as being 6.5×10^{-4} mol cm^{-3} LiCl. This is the amount of additional LiCl which can be accommodated within a 1.8 M $LiAlCl_4$ solution without precipitation based on previous results [10]. The value of D was found to increase with deposit thickness, as expected; however, the value for glassy carbon, 1×10^{-7} cm s^{-1} indicates that the surface is not wholy active. Diffusion coefficients for Li^+ in $SOCl_2$ have not been reported in the literature, so an accurate assessment of the active electrode area [16] cannot be made with certainty. However, assuming a value of 1.3×10^{-5} cm s^{-1} which is characteristic of Li^+ in 1.0 M LiCl aqueous solution, it seems that less than 1% of the surface is active for $SOCl_2$ reduction. It must also be borne in mind that these diffusion coefficients were calculated from results based on the 'sandwich' type cells employed in this work. More realistic results would be expected using cathodes in open cells, without the complication of the ceramic separator. Knowing the surface area of Shawinigan carbon black to be 60 m^2 g^{-1}, the area-

Table 1. Values of apparent and area-corrected diffusion coefficients for a variety of cathodes

Cathode employed	*Apparent diffusion coefficient (D) (cm^2 s^{-1})*	*Diffusion coefficient (area corrected) (cm^2 s^{-1})*
Glassy carbon	1.06×10^{-7}	1.06×10^{-7}
Porous carbon, 50 μm	3.06×10^{-5}	8.97×10^{-11}
Porous carbon, 100 μm	9.12×10^{-5}	6.54×10^{-11}
Porous carbon, 200 μm	2.17×10^{-4}	3.90×10^{-11}
Porous carbon, 300 μm	3.64×10^{-4}	2.90×10^{-11}
Porous carbon, 400 μm	5.55×10^{-4}	2.51×10^{-11}
Porous carbon, 500 μm	5.88×10^{-4}	1.69×10^{-11}
Porous carbon, 600 μm	6.46×10^{-4}	1.29×10^{-11}

corrected diffusion coefficients for porous carbon cathodes could be calculated. These, however, were found to be very small; therefore, most of this surface is unavailable for LiCl deposition.

4. Conclusions

1. Earlier findings that the reduction of $SOCl_2$ at a carbon surface is controlled by the solubility of LiCl in the electrolyte immediately surrounding the electrode were confirmed.
2. The electrode remains active until the LiCl is unable to leave the electrode by diffusion.
3. On standing in the cell after passivation, a glassy carbon cathode recovers capacity for further reduction of $SOCl_2$, as the LiCl product is removed into the bulk solution. This occurs to a lesser extent with porous carbon cathodes.
4. About 1% of a glassy carbon surface is active for the reduction process; at a porous carbon cathode only a very small fraction of the calculated surface area is active.
5. There exists a porous carbon black electrode thickness above which the reaction time is unaffected by thickness increases. This thickness is greater for lower current densities.

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