# RATE LIMITING MECHANISMS IN LITHIUM–MOLYBDENUM DISULFIDE BATTERIES

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## Summary

Considerable effort has been devoted in recent years to the development of practical, secondary lithium batteries using intercalation cathodes. One limitation of many of these batteries has been their relatively low power densities. Significant progress has been made towards alleviating this limitation in cells utilizing lithium–molybdenum disulfide technology.

Frequency response analysis has proven to be a powerful tool for use in studying rate limitation mechanisms in cells. For the lithium–molybdenum disulfide system as developed in this laboratory, we have found that diffusion-related contributions to cell impedance, and interfacial and resistive contributions to cell impedance, can be readily segregated by virtue of the fact that the diffusion-controlled mechanisms dominate the low frequency end of the impedance spectra whereas the other mechanisms dominate the high frequency end.

In this paper we report on a study of rate limitations at the high end of the frequency spectrum in lithium–molybdenum disulfide cathodes. We have identified and quantified in these cathodes, using a transmission line model, impedance elements corresponding to electrolyte impedance, a cathode grain/electrolyte interface impedance, and a grain-to-grain contact impedance that includes both a resistive and a capacitive element.

## 1. Introduction

Molybdenum disulfide has been studied by a number of investigators in the past and was found to have only limited utility as a cathode active material [1]. Workers in this laboratory, and at the University of British Columbia, have shown that structurally modified molybdenum disulfide has much greater utility as a cathode active material [2]. It has also been shown that the structurally modified material is stabilized by the presence of added electrons within the conduction band of the material [3]. This stabilization,

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in the case of lithiated molybdenum disulfide, is provided by the electrons which provide charge compensation for intercalated lithium ions. This structurally modified material was used to fabricate the electrodes used for this study. A variety of cathodes was constructed with the aim of studying limiting cases where the transmission line model used to interpret the a.c. impedance data obtained could be reduced to a simple form.

## 2. Theory

The model used to represent the experimental cathodes is shown schematically in Fig. 1. The cathode particles are represented by discs which are stacked atop one another. There is an electronic impedance associated with the contacts between the discs and between the stack and the current collector located at one end of the stacks. Electrolyte permeates the spaces between the stacks and there is an electrolyte resistance, associated with the ion conductivity between the open end of the stacks and the cathode particle in question, which is proportional to the electrolyte path length. The cathode particle/electrolyte interface impedance is inversely proportional to the area of the exposed edges of the discs.

A finite continuous transmission line was used to mathematically represent the model. Implicit in this representation is the assumption that the size of each particle is small in comparison with the cathode thickness. The transmission line circuit is shown in Fig. 2. The sum of the contact impedances in a stack is represented by a contact resistance, $R_C$, and a contact capacitance, $C_C$. The electrolyte resistance in the pores between
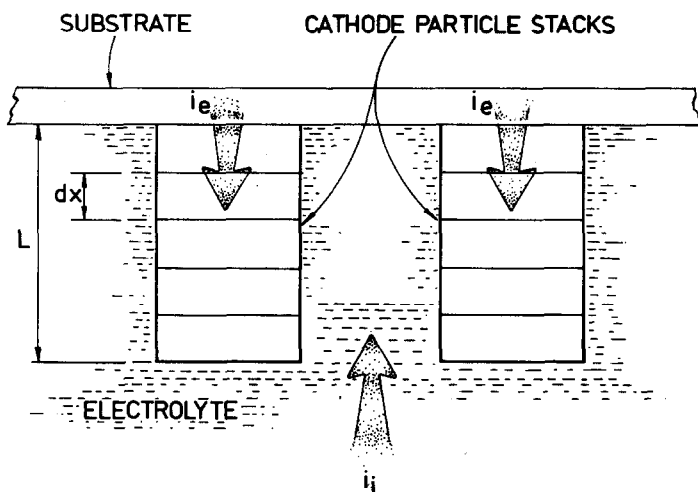


Fig. 1. The diagram illustrates the model used to describe experimental cathodes. The ion current, $i_i$, penetrates electrolyte-filled pores between cathode particle stacks of height $L$. The electron current, $i_e$, passes from the current carrying substrate along the particle stacks. The particle thickness is $dx$.
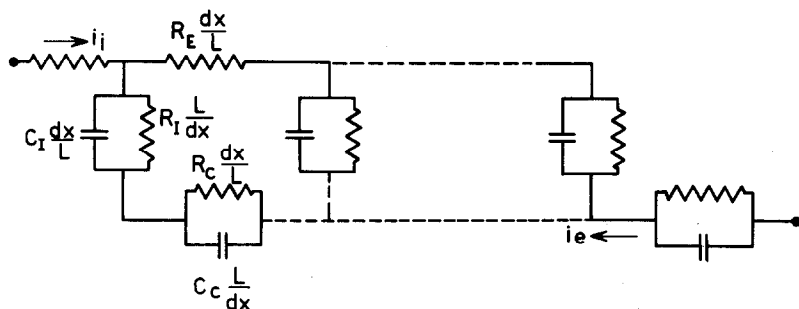
Fig. 2. A finite continuous transmission line representation for the cathode model. The symbols are defined in Fig. 1 and in the text.

stacks is represented by $R_E$ and the interface impedance in a stack is represented by a resistive element $R_I$ and a capacitive element $C_I$.

The cathode impedance, as measured between a reference electrode at the cathode/electrolyte surface and the cathode current collector, is then given by:

$$Z(\omega) = \frac{Z_1 Z_2}{(Z_1 + Z_2)} + \frac{1}{2}\{Z_i(Z_1 + Z_2)\}^{1/2}\left[\left(\frac{Z_1 - Z_2}{Z_1 + Z_2}\right)^2 \tanh \frac{1}{2}\left(\frac{Z_1 + Z_2}{Z_i}\right)^{1/2} + \right.$$

$$\left. + \coth \frac{1}{2}\left(\frac{Z_1 + Z_2}{Z_i}\right)^{1/2}\right] \tag{1}$$

where $Z_1 = R_E$, $Z_2 = R_C/j\omega R_C C_C + 1$, $Z_i = R_I/j\omega R_I C_I + 1$. The major refinement of this model over that given in the literature by de Levie [4] and others is the inclusion of elements to represent the contact impedance.

The general expression can be simplified considerably in certain limits. These are as follows:

(a) In the limit where the interface impedance is substantially greater than either the electrolyte impedance or the contact impedance, such as would be the case with very thin electrodes, the cathode impedance is given by:

$$Z(\omega) = \frac{R_I}{j\omega R_I C_I + 1} \tag{2}$$

(b) In the limit of high frequency, and if $C_C \ll C_I$, the cathode impedance is approximately equal to a parallel combination of the contact impedance and the electrolyte impedance and is given by:

$$Z(\omega) = \frac{R_C}{j\omega R_C C_C + 1 + R_C/R_E} \tag{3}$$

## 3. Experimental

The cathodes evaluated in this study were fabricated using structurally modified molybdenum disulfide bonded to a flat current collector. The thickness and density of the electrodes were varied to suit the experimental requirements. Because of the difficulty of providing a reference electrode that adequately measures a reference potential, it was decided to work with cells consisting of two identical cathodes separated by a 25 $\mu$m thick porous, polypropylene separator. The cathodes were lithiated as a single electrode, and the single electrode was cut in half to produce the cathodes used in the experimental cells. The cathodes had an area of 1.44 cm$^2$ each, and the data obtained were thus for two such cathodes in series, or equivalently, for a single cathode of area 0.72 cm$^2$.

For the purpose of this study, an electrolyte consisting of various concentrations of LiAsF$_6$ in propylene carbonate was used. Thus the electrolyte conductivity could be related to published bulk values for dilute electrolytes where effects due to the anion can be neglected [5]. The experimental cells were hermetically sealed.

The impedance measurements were obtained using a Solartron Model 1170 frequency response analyzer coupled to a Compupro 8 bit microcomputer. A Stonehart model BC 1200 potentiostat was used to interface the cell to the frequency response analyzer.

## 4. Results and discussion

To facilitate identification of the interface impedance as defined within the model, the impedance spectrum of a thin cathode having large molybdenum disulfide grains was measured. In this case the contact impedance could be neglected because the density of grain-to-grain contacts within the cathode was small. The use of grains with a relatively large average diameter of 80 $\mu$m further assured that the electrolyte pores were sufficiently short and of sufficiently large diameter for the electrolyte resistance within the cathode to be neglected also. The spectrum for the thin cathode is shown in Fig. 3. The theoretical impedance values were computer generated using an extended model including a diffusion term which gives, below 0.2 Hz, slightly different values from the model defined in the text.

The electrolyte resistance in the separator between the cathodes was also determined from the offset on the real axis of the cathode impedance spectrum for a cathode immersed in an electrolyte consisting of 0.1M LiAsF$_6$ in propylene carbonate in the high frequency limit.

The temperature dependence of both the interface impedance and the electrolyte resistance were found to exhibit an Arrhenius behaviour. These data are shown in Fig. 4. The activation energies for the resistive component of the interface impedance and the electrolyte resistance were determined, respectively, to be 0.48 eV and 0.15 eV. In the case of the electrolyte resis-
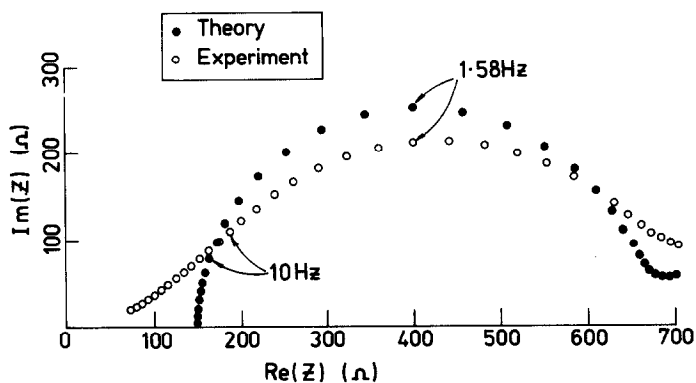
Fig. 3. An a.c. impedance spectrum for a thin cathode taken at $-20\,^{\circ}C$. The data density is 10 points per decade.
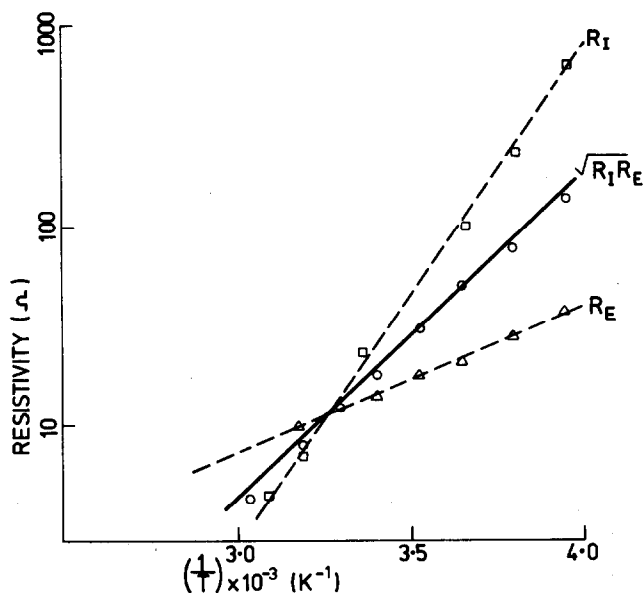


Fig. 4. Arrhenius plots for $R_E$, $R_I$, and $(R_E R_I)^{1/2}$. The solid line drawn through the data for $(R_E R_I)^{1/2}$ has a slope equal to the average of the slopes determined independently for $R_E$ and $R_I$ from the dashed lines.

tance, the activation energy was found to be in agreement with that reported for bulk electrolyte [6].

We were able to use the Arrhenius behaviour of the determined impedances to compare impedances in different cathodes. The absolute values of impedances in different cathodes cannot be directly compared because they have varying geometrical parameters. However, these parameters do not enter into the activation energies for the impedances and thus a direct comparison can be made between activation energies in different cathodes.
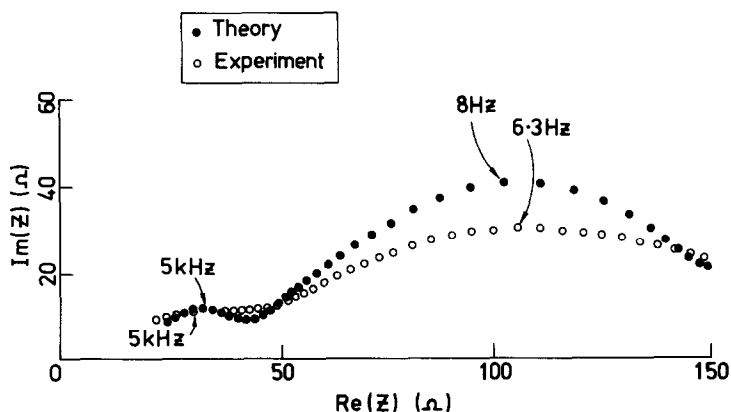
Fig. 5. An a.c. impedance spectrum for a thick cathode taken at −20 °C. The data density is 10 points per decade.

TABLE 1

Typical cathode impedance parameters at 25 °C and at −20 °C

| Temp. (°C) | $R_E$ ($\Omega$) | $R_I$ ($\Omega$) | $C_I$ ($\mu$F) | $R_C$ ($\Omega$) | $C_C$ ($\mu$F) |
|---|---|---|---|---|---|
| 25 | 60 | 6 | 300 | 9 | 2.0 |
| −20 | 150 | 70 | 350 | 20 | 2.0 |

An impedance spectrum was measured for a thick cathode where each of the interface, contact, and electrolyte impedances are significant. The spectrum, obtained at −20 °C and shown in Fig. 5, has two distinct features separated by a minimum in the imaginary component at about 700 Hz. We identified the high frequency part of the spectrum as being attributable to contact impedance and the low frequency part as being dominated by the interface and electrolyte impedances. Our model reduces to that of de Levie if the contact impedance is assumed to be zero, and if de Levie's model is used to fit to the lower frequency data, the width of the spectrum on the real axis between minima in the imaginary component of the impedance is given by the geometric mean of the interface resistance and the electrolyte resistance. The temperature dependence of this parameter, shown in Fig. 4, was found to exhibit an Arrhenius behaviour, with an activation energy equal to the average of that independently determined for the electrolyte and interface impedances. Thus the identification of the low frequency portion of the spectrum with the interface and electrolyte resistances was established.

By virtue of the fact that the magnitude of the high frequency portion of the spectrum is considerably smaller than the determined magnitude of the electrolyte impedance, and by using eqn. (3) with $R_C/R_E \ll 1$, it is seen that this portion of the spectrum depends only on the contact resistance.

The necessary condition that $C_C \ll C_I$ was experimentally determined to hold true (see Table 1). The contact impedance was observed to have no significant temperature dependence.

Additional spectra were obtained at +25 °C. In this case the distinctive features of the spectrum are absent because of the changes of the various impedance parameters with temperature, but the complete model could be used to obtain a fit of the data to the parameters. Table 1 shows typical cathode impedance parameters at 25 °C and at −20 °C.

## Conclusion

The contributions above 1 Hz to cathode impedance in molybdenum disulfide cathodes as developed in our laboratory were determined. At 25 °C, the impedance is dominated by the resistance of the electrolyte in the cathode pores, but as the temperature is reduced the cathode/electrolyte interface impedance becomes increasingly large. It is expected that this interface impedance determines overall cathode impedance at temperatures significantly below −20 °C. The results indicate that improvements in low-temperature pulse rate capability in cells using these cathodes will come about through modification of the cathode/electrolyte interface, and to a lesser extent, to improvement in low temperature electrolyte conductivities.

## Acknowledgments

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