

Electrochemical Impedance Spectroscopy and its Applications to Lithium Ion Cells

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ABSTRACT

Electrochemical impedance spectroscopy (EIS) is a non-destructive technique often used to understand the interfacial behavior in electrochemical systems. The ability of the technique to segregate various processes, i.e., ohmic conduction, charge transfer, interfacial charging, mass transfer etc, makes it an elegant technique for electrochemical systems. Its applicability to lithium ion cells is further enhanced by the fact that both the electrodes, especially the carbon anode, are covered by surface films. This paper describes the EIS response of individual electrodes in the lithium ion cells under variety of experimental conditions, i.e., temperature, high temperature storage and cycling.

1.0 INTRODUCTION

Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for understanding electrochemical systems. Briefly, this technique involves a determination of cell impedance, in response to a small (~5 mV amplitude) ac signal at any constant DC potential (preferably at the OCV to minimize the Dc currents), over a span of frequencies ranging typically from 10^5 KHz to 10^{-3} Hz (hence the term impedance spectroscopy). From the measured cell impedance in the form of real and imaginary components and phase angle, it is possible to examine and qualitatively determine several processes such as the electronic/ionic conduction in the electrode and electrolytes, interfacial charging either at the surface films or the double-layer, charge transfer processes and the mass transfer effects, if any. The time constants for these different processes being different, their features will show up at different frequencies in the EIS spectra. The advantages of this techniques include: 1) its non-destructive nature, since the polarization applied is low enough that linear polarization conditions (i.e., where the polarization increases linearly with current) are maintained and the rate equations are simplified accordingly, 2) rapid and easy measurement methods as presently possible with the advent of computer-controlled equipment such as potentiostats and frequency response analyzers and appropriate software, which enormously simplify the data collection as well as subsequent analyses. The deficiency of this technique, on the other hand, is mainly related to the difficulty in interpreting the data, i.e., in envisaging a suitable electrical equivalent circuit to represent the electrochemical system and in

quantitatively determining the relevant electrical parameters that would help understand the response of system.

Historically, this technique has been applied to a variety of electrochemical systems. Specifically, it has been used in understanding the adsorption of (neutral) molecules and passive films on electrode surfaces, determining the efficacy of corrosion inhibitor coatings and in monitoring the energy conversion devices, i.e., batteries and fuel cells. With respect to batteries, this technique has been used, successfully in many systems, to estimate the state of charge non-destructively. More quantitatively, this technique has been used to determine the electrochemical reaction rates, including corrosion currents, and to measure the ionic conductivity of electrolytes or thin films of polymers. In the case of lithium primary cells, this technique has enabled probing of the surface films that affect the voltage delay and shelf life characteristics.

2.0 LITHIUM ION CELLS

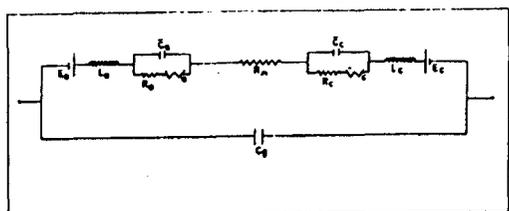
Lithium ion rechargeable cells involve intercalation reactions at both the anode and the cathode, which involve minimal morphological changes in the electrode, unlike the dissolution-precipitation processes. Yet the electrode/electrolyte interfaces sustain noticeable changes during charge-discharge cycling, mainly due to the surface films on both the electrodes. The surface films, formed on the anode in the first lithiation step to provide the desired kinetic stability to the electrolyte towards both the electrodes, continue to grow during charge-discharge cycling. Since the charge transfer processes

corresponding to lithium intercalation and deintercalation occur through the film-covered electrodes, the film characteristics, especially its thickness and resistance, play a significant role in the rate capability and overall performance of the cell.

Various techniques are being used to examine the nature of the surface films on carbon, including the direct, often in-situ techniques such as FTIR, Raman spectroscopy and optical methods such as AFM, TEM and ellipsometry. These methods are highly informative about the chemical nature of the films; however, they are adaptable to real cells. Electrochemical impedance spectroscopy, on the other hand, is easier to adopt even on sealed cells and will provide useful information on the interfacial impedance and its changes.

We, at JPL, have been evaluating various lithium ion prototype cells, of high capacity (4-40 Ah) and developed for aerospace applications under NASA-DoD joint effort. Our evaluation protocol consists of characterization of performance at various rates of charge and discharge at different temperatures and determination of cycle life at different temperatures and of storage characteristics. During these studies, we have routinely used electrochemical impedance spectroscopy to determine the cell impedance characteristics.

The cell impedance has contributions from individual electrodes and as well from other components such as electrolyte and leads. A generalized equivalent circuit for a two-terminal device¹ is shown in Fig. 1.



E_0, E_c = Single electrode potentials. W_0, W_c = Diffusional (Warburg) impedances.
 L_0, L_c = Lead inductances. R_m = Resistance of solution and separator.
 C_0, C_c = Double layer capacitances. C_g = Inter-electrode capacitance.
 R_0, R_c = Charge transfer resistances.

Fig. 1 Generalized equivalent circuit of a cell.

There is a geometric capacitance arising out of the two dissimilar electrodes, which are in parallel with each other. In addition, each of electrodes' impedance response includes: 1) an inductive component from leads and from the electrode materials, 2) a double-layer capacitance at the electrode/electrolyte interface, 3) a charge transfer resistance representing the activation

process and 4) a Warburg impedance to represent the mass transfer effects interfering with the charge transfer processes. In other words, each of the electrode impedances are represented by the well-known Randles' circuit,² which is applicable only if the electrodes are free of any surface passive films. However, in the case of lithium ion cells, we know that surface films (SEI) exist, especially at the carbon anodes, and to some extent on the metal oxide cathodes. The equivalent circuit may therefore be modified accordingly.

2.1 AC Impedance of Lithium Ion cells

A typical EIS plot of a graphite anode in lithium ion battery electrolytes, e.g., 1 M LiPF₆ in an equi-proportion mixture of ethylene, diethyl and dimethyl carbonates, is shown in Fig. 2.

The above pattern is much similar to a charge transfer over film-covered electrode, with interference from mass transfer effects. This is consistent with the current understanding of the graphite anode in that it is covered with an SEI, which is formed from the reactions involving the reductions of electrolyte species and also prevents hinders these processes.

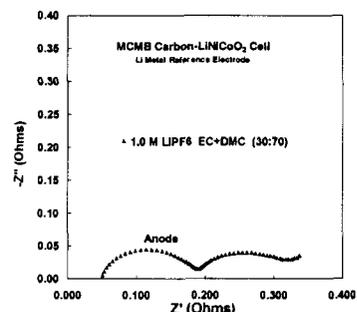


Fig. 2 Typical EIS plot of the graphite anode.

The relaxation loop evident at high frequencies may thus be attributed to the charging of the SEI and the SEI characteristics, i.e., its resistance and capacitance may be deduced from the high frequency relaxation. Such an assignment may be further confirmed by the changes in SEI under different experimental conditions, e.g., temperature, and ageing. The second relaxation loop may be attributed to the charge transfer process on the SEI-covered electrode and the corresponding rate parameters, capacitance of the SEI/electrolyte double-layer and the charge transfer resistance may be deduced from it.³ The mass transfer effects, if prominent in the impedance data,

may be attributed to the slow solid-state diffusion of lithium in the graphite lattice. Both the SEI characteristics and the charge transfer kinetics at the carbon anode are highly dependent on the nature of electrolyte. Accordingly, we have routinely been using the EIS technique at JPL to understand the film-forming nature of the electrolytes with different solvents.

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The EIS pattern of the cathodes is much like the anode, as shown in Fig. 3.

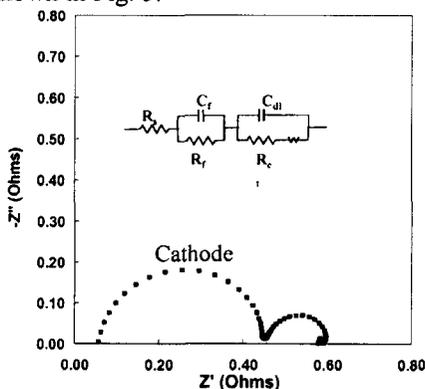


Fig. 3: EIS spectrum of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode.

In the case of cathode also, there are two relaxation loops, as may be expected from the presence of a surface layer, similar to the SEI on the anode, on the cathode as well. Again, assigning the high frequency loop to the surface film and the low frequency loop to the charge transfer kinetics with possible interference (not significant in this case) from mass transfer, it is possible to infer useful information on the surface film characteristics as well as the reaction rates from the impedance spectra.

With both the impedance patterns of the anode as well as the cathode being complicated by the presence of the surface films, the overall impedance of the cell is sufficiently complex to be decomposed into individual electrode contributions. In order to understand the impedance behavior of individual electrodes, we have fabricated three-electrode cells. Here, we have adopted a strategy that helps us understand the impedance characteristics of several sealed prototype lithium ion cells. We have fabricated cells with the same electrodes (but smaller) being used by the industrial partner. The ratio of the anode to cathode capacities are also maintained the same as the sealed prototype cells. The laboratory cells (~400 mAh) are, thus, similar to the prototype cells, but for a relatively higher electrolyte content. In addition, we have incorporated a lithium reference electrode to measure the impedance characteristics of the individual electrodes as well as the cell. Figure 4 shows the EIS patterns of the anode and the cathode against the lithium reference electrode, and the cell impedance, which is compared with the sum of the anode and the cathode contributions.

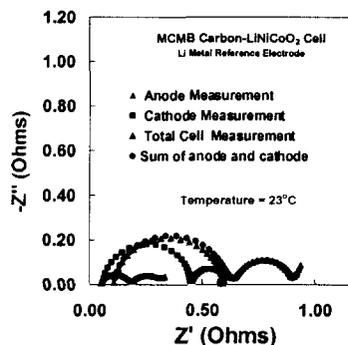


Fig. 4 : EIS patterns of a Li ion cell compared with the sum of individual electrode impedances.

As may be seen from the figure, the sum of the cathode and anode impedances matches well with the observed cell impedance. Further, the cathode impedance

seems to contribute a significant portion of the cell impedance. The anode contribution, on the other hand, is smaller and seems to disappear at low frequencies. This is quite contrary to what was observed by the research group at Sony,⁴ which in turn implies that the method of electrode coating, loading, particle size and porosity dictate the relative kinetics of lithiation at anode and cathode.

The above inference of cathode contributing more towards the cell impedance is also supported by our DC polarization studies. Fig. 5 shows the Tafel polarizations curves of both $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode and graphite anode in our laboratory cell, at slow scan rates. As may be seen from the figure, the graphite anode sustains higher currents, almost an order of magnitude higher, than the nickel cobalt oxide cathode. The polarization of the anode is relatively small compared to that of the cathode over a good margin of currents.

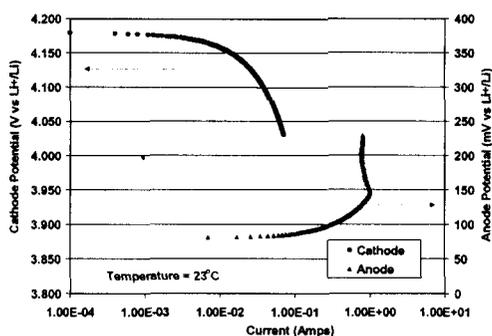


Fig. 5 DC polarizations of cathode and anode.

3.0 EIS UNDER DIFFERENT CONDITIONS

Based on the above understanding relative to interpreting the EIS patterns of lithium ion cells, we have been using this technique to monitor the cell and electrode impedance characteristics under various experimental conditions. A few of such cases are described below:

3.1.1 EIS at low temperatures

Low temperature performance is a critical for several of NASA's planetary missions. The research effort at JPL over the last decade have focused mainly on this aspect and considerable improvements have been made in this category via optimizing the solvents that would provide good ionic conductivity at low temperatures and yet have good filming properties.⁵⁻⁸ As mentioned before, EIS technique is being routinely use d

to understand the SEI characteristics as a function of solvent compositions and temperature. Fig.6 illustrate the changes in the cell and individual electrode impedances at 0°C and -40°C .

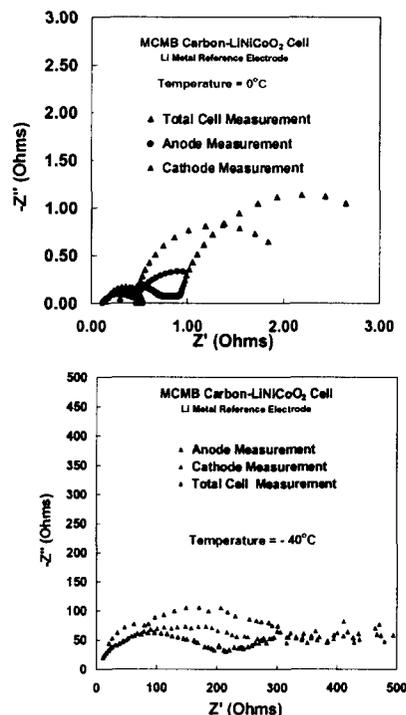


Fig. 6. EIS patterns of Li ion cells at 0°C and -40°C .

As may be seen from the figures, the anode contribution is relatively more at 0°C , compared at room temperature, but is still less than that of the cathode. At a lower temperature of -40°C , however, the impedance arising from the anode SEI is comparable to that of the cathode surface layer. In other words, there is a change over in the rate determining process, as we approach low temperatures, below -20°C . The DC polarization studies performed under these conditions confirm that the anode kinetics do get hindered significantly at low temperatures such that they could be rate limiting. This underlines the significance of suitable electrolyte characteristics for a good low temperature performance.

3.1.2. EIS During High Temperature Storage

The ability of Li ion cells to withstand high temperatures (over 40°C) is another requirement for some aerospace applications. Similar to the low temperature performance, the high temperature tolerance is also

strongly dependent on the SEI characteristics, which in turn are dictated by the electrolyte composition. Again, using EIS technique, we examined the interfacial conditions on both anode and cathode during exposure to high temperatures.⁹ Fig. 7A and 7B shows the variation of EIS behavior of the anode and the cathode before and after one-week storage at 60°C. These measurements were made at the same SOC, i.e., the cells were charged fully subsequent to self-discharge.

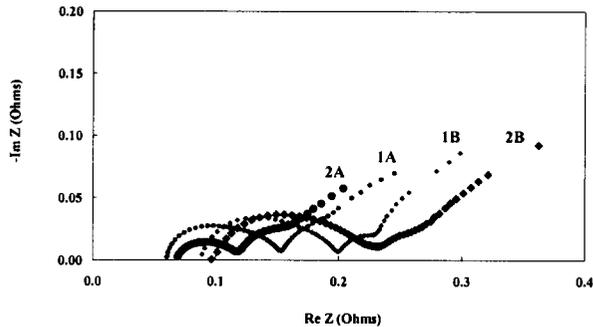


Fig. 7A: EIS plots of graphite anode in 1) high EC content and 2) EC:EMC:DMC solutions A) before and B) after storage at 60°C for one week.

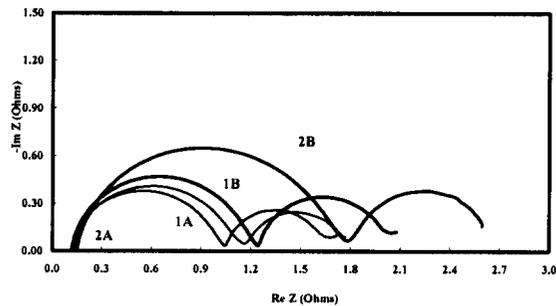


Fig. 7B EIS plots of Li-C/LiNi_{1-x}Co_xO₂ cells in 1) high EC content and 2) EC:EMC:DMC solutions A) before and B) after storage at 60°C for one week.

For the sake of clarity, data for only two electrolytes are shown here and the data from the third electrolyte follow similar trend. As may be seen from the figures, the cell impedance as well as the cathode and anode impedances grow during the high temperature storage. These ac impedance data were analyzed using equivalent circuits described above (Section 2), consisting of a electrolyte resistance in series with a parallel combination of capacitance and resistance representing the surface film and another parallel

combination of capacitance (double-layer) and resistance (charge transfer) to represent the faradaic process. Analyses of the above data indicate that the SEI on the graphite is still intact and also grows further during high temperature storage, contrary to some reports in the literature that it would dissolve at high temperatures.¹¹ Further tests to confirm this are in progress. Also, much like the SEI on the cathode, the resistance of the SEI on the LiNi_yCo_{1-y}O₂ cathode increases during the above high temperature storage, i.e., the SEI builds on both the anode and cathode. In other words, the interfacial impedance increases at both the anode and cathode, thus contributing to a build-up of cell impedance during storage, which in turn results in a permanent capacity loss upon storage.

3.1.3 EIS during cycling

As mentioned before, the changes in the EIS characteristics of the sealed prototype cells have also been measured during cycling. The assignment in this case is, however, not as certain, due to the absence of lithium reference electrode. Nevertheless, reasonable extrapolations may be made, based on the behavior of individual electrode as above.

Fig. 8 shows the typical impedance plots of lithium ion cells in the course of cycling. There is in general a gradual increase in the cell impedance as a function of cycling.

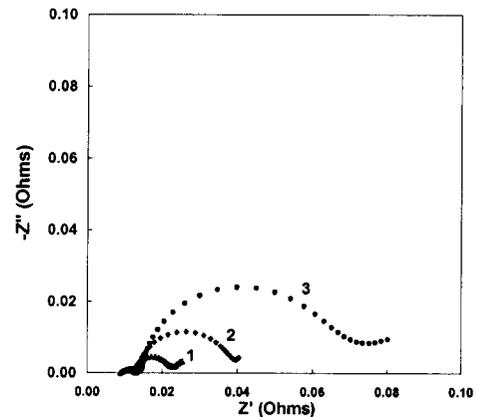


Fig. 8. EIS plots of Li ion cells after 1) 5, 2) 100 and 3) 200 cycles at 25°C.

There is a small increase in the series (Ohmic) resistance but a relatively larger increase in the relaxation loop, especially at the low frequency process. Combining these results with the three-electrode measurements, it is reasonable to assume that the cathode contribution is a significant portion to growth of cell impedance during

cycling. It would, however, be more prudent to draw conclusions from cycling of half-cells as done for storage.

4.0 CONCLUSIONS

The EIS technique could be used to follow the interfacial changes occurring in the batteries at both the electrodes. In the case of lithium ion cells, both the electrodes are covered with surface films, which are ionically conducting and over which electrochemical charge transfer processes occur. The impedance in the prototype cells is mostly dominated by the metal oxide cathode at ambient temperatures. At low temperatures, approaching -40°C , the anode kinetics appears to become more sluggish compared to the cathode kinetics. EIS data will also provide useful information on the interfacial degradation during cycling or storage (especially at high temperature) of lithium ion cells.

5.0 ACKNOWLEDGEMENTS

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