TEMPERATURE DEPENDENCE OF DOUBLE LAYER CAPACITANCE IN LITHIUM-ION BATTERY

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Abstract - Temperature plays an important role on the performance of a lithium-ion battery. The results of the experimental study of the double layer capacitance were presented. The double layer capacitance in the cathode interface during discharging process has been identified at wide range of temperatures from 50ºC to -20ºC from series of impedance measurements at different state of charge conditions. Results proved that at higher temperatures, the cathodic double layer capacitance is higher than at lower temperatures.

Index Terms - Performance of lithium-ion battery, double layer capacitance, temperature effects in lithium-ion battery.

INTRODUCTION

Lithium ion batteries have found wide applications in powering devices in electronics, biomechanics, automotive and power generation industries and many others [1-4]. In the last two decades, capacity and temperature range of operation of lithium-ion battery have been improving significantly and cost of the batteries has been coming down substantially as well. However, at subzero temperatures capacity and power availability decrease noticeably and it has still been a challenge for the batteries manufacturers and researchers to overcome [5]. Therefore, there is a need to understand and provide resolution. One of the techniques used in the electrochemical analysis is an Electrochemical Impedance Spectroscopy (EIS). It has been used to identify interfacial behavior of electrochemical systems by using a proper equivalent circuit of the system [6, 7]. This contribution is a continuation of our work where cathode and anode interfacial resistances have been identified at a wide range of temperatures by using electrochemical impedance spectroscopy tool and a simple equivalent circuit of lithium-ion battery (Figure 1) [8]. In this contribution, the double layer capacitance of the model in cathode side has been identified and investigated. The electric double layer capacitance is the potential difference across an interface (cathode or anode) and change of its value can produce the change in electrodes' electrochemical processes [9, 10]. The effects of temperature on its value has been investigated and analyzed in this contribution.

II. EXPERIMENTAL SETUPS

The experimental study was conducted at CAVID Hybrid Electric Applied Research Laboratory at Western Michigan University. The test cell used was $LiFePO_4$ based prismatic type with nominal capacity 20Ah and nominal voltage 3.3V. The electrochemical impedance measurements was carried out using AMREL impedance meter, model FCL-10-100 at different battery cell temperatures and state of charges. This particular model had the frequency range from 0.1 Hz - 20000 Hz and a built-in interface software. The different temperatures from -20 ºC to 50 ºC of the battery cell were maintained by Sun System's environment chamber, model EC1x during the experimentations. The charging and discharging of the battery cell were carried out using ARBIN battery tester model BT2000. The basic measurement tests were conducted prior to running the impedance tests. The battery terminals' connectors were specially made of Cu in house to avoid any additional resistances. Figure 2 showed the impedance meter and battery connections.

III. METHODOLOGY

The impedance measurements were carried out at different state of charges (SOC) of the battery cell maintaining constant temperature. The temperatures of $LiFePO_4$ cell were varied from 50ºC to -20ºC using the environment chamber. The state of charges as a function of voltage at different temperatures were identified from capacity and open circuit voltage tests [5]. During frequency sweep the cell was discharged at 5 Amps which was recommended discharge current value for the particular impedance meter used for good data accuracy. Figure 3 showed a Nyquist plot of a lithium-ion battery and parameters utilized to calculate the double layer capacitance in the cathode side.
During the experimentations, the Nyquist plots were generated for all cases using the data points and interface software of the impendence meter used. The impedance frequency swept for 0.1 Hz to 20 kHz was conducted in each experiment. The double layer capacitance in cathode side can be calculated by the following equation [10,11]:

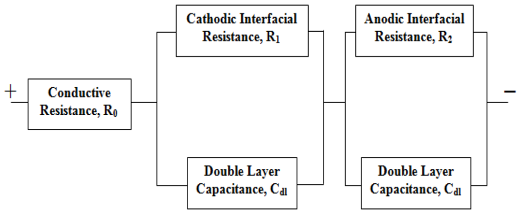

Figure 1: The equivalent circuit model of lithium ion battery [9,10].

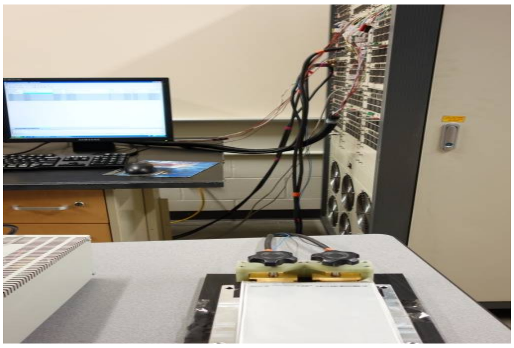

Figure 2: The experimental set up and battery connectors

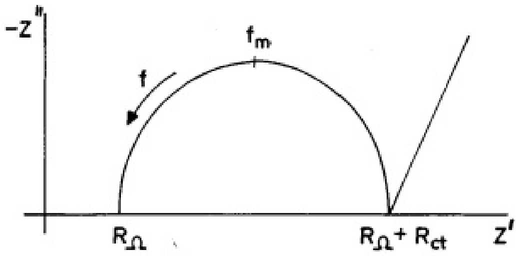

Figure 3: A sample nyquist plot of lithium ion battery

$$C_{dl} = \frac{1}{(2\pi f_m R)} \qquad (1)$$

Where,
C_{dl}, double layer capacitance f_m, frequency at the peak point of the semicircle as shown in Figure 3. R, cathodic or anodic interfacial resistance which is R_{ct} in Figure 3 and whereas R_{Ω} is the ohmic resistance. The ZView software had been used to extract cathode interfacial resistance, R at different temperatures by using the equivalent circuit (Figure 1) and f_m had been identified from raw data of impedance measurements.

IV. RESULTS AND DISCUSSIONS

Experiments were carried out using the test cell at different temperatures and state of charges (SOC) of the battery and corresponding Nyquist plots were generated. Figure 4 was one of those plots shown at the temperature of 25 °C from ref. [8]. The internal resistances of the test cell increased at the lower SOCs as expected and the values were comparable with other reported researches [12, 13]. The internal resistance changes as a function of tempeartures of the battery cell was illustrated in Figure 5 at 50% SOC. The conductive resistance (R0)of the battery was comparatively low in comparision to other resistacnes as seen in Figure 5 and it was mostly constant for all the tempartures tested at about 1 mΩ, though the anodice (R1) and cathodic (R2) resistances were incresed substantailly as the temperature decreased. In fact the cathodic resistance increased by 13 times from 50 ºC to -20 ºC. For this chemestry battery, it can be seen that there was a sweet zone where the resistacne chagnes very little at the temparture ranges from 50 ºC to 10 ºC.

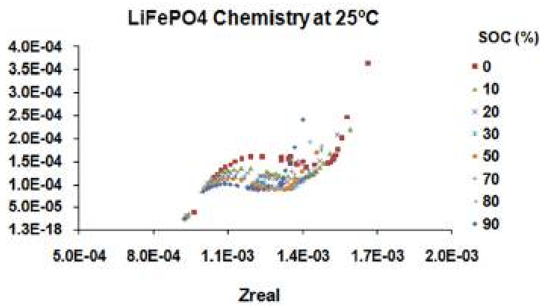

Figure 4: Nyquist plots of the test cell at various SOC [8]

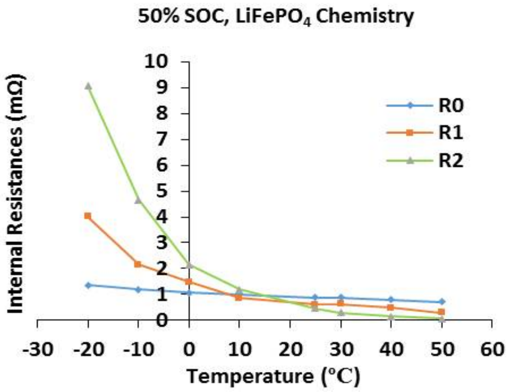

Figure 5: Internal resistacnes vs temparature at 50% SOC [8]

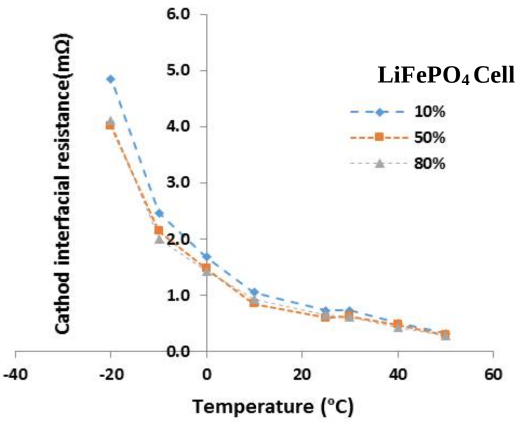

Figure 6: The cathodic resistances vs temperatures for various SOCs [8].

In Figures 6 and 7, the cathodic and anodic resistances were illustrated at different SOCs for various temperature changes. At lower SOCs, the cathodic resistances were higher for the all temperatures as expected. The similar trend was also observed for the anodic resistances as well in Figure 7. It also can be seen that the anodic resistances were higher in comparison to the corresponding cathodic resistances at lower experimental temperatures.

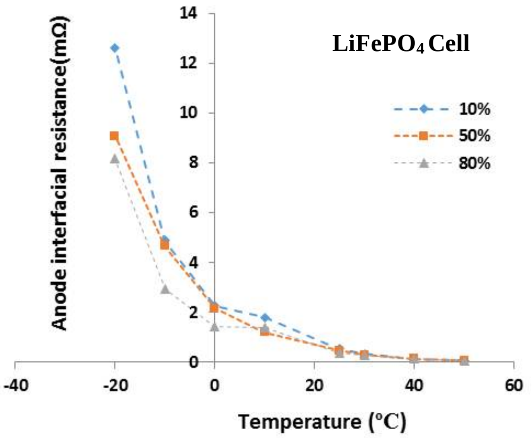

Figure 7: The anodic resistances vs temparatures for different SOCs [8].

The double layer capacitance at three different state of charges, 10%, 50% and 80% had been plotted in Figure 8. Capacitance values had been calculated only in cathode interface due to frequency limitation of the impedance meter to 0.1 Hz. In the Nyquist plots, the most part of the second semicircle missed. In ref. [8], anodic interfacial resistance was identified by using ZView software. But it was unclear to find out peak frequency of the missing semicircle. The value of the double capacitances for three SOCs at different temperatures were also given in Table 1. At every state of charge (SOC) the double layer capacitance increased as temperature increased. At -20ºC and 50% state of charge its value was 7 F when at 50ºC it increased to 66 F which was almost 900% increase of capacitance.

At the lower temperatures, the capacitance values were almost similar for different state of charges showing that SOC has a little influence on it. As it can be seen from figures that the capacitance decreases as temperature decreased which was an opposite trend of the resistances as expected. At the temperature changes from 0 ºC to 50 ºC the capacitance of the cell had increased more for the higher SOC of the battery cell. In fact, there were 10.8, 13.2 and 17.75 times increased in capacitance values for 10%, 50% and 80% SOCs, respectively for the experiment considered. It can be seen that at the higher temperature the rate of capacitance increased was higher for the lower SOC conditions. In fact at 50 ºC the rate of capacitance increased per unit of SOC was about 30% for 10% to 50% SOC conditions and its value decreased to 16.7% for the 50% to 80% SOC conditions. Though for other lower temperature values, it fluctuated. Therefore, it is recommended/planned to do more research in this area in future.

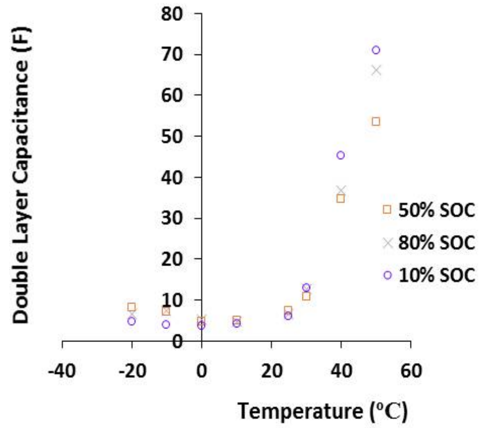

Figure 8: The double layer capacitance at different SOC for various temperatures.

Temp (ºC)	SOC (%)		
	10	50	80
	Double Layer Capacitance (Cathode Side, Discharge Process), F	Double Layer Capacitance (Cathode Side, Discharge Process), F	Double Layer Capacitance (Cathode Side, Discharge Process), F
50	54	66	71
40	35	37	45
30	11	13	13
25	7	7	6
10	5	5	4
0	5	5	4
-10	7	7	4
-20	8	7	5

Table 1: The double layer capacitance values.

The double layer capacitance characterizes by the size and microstructure of the electrode material [14-17]. The positive and negative charged particles are accumulated very close to the boundary of the electrode interface and make a double layer. This is the reason it is called a double layer. The minimum distance between these two layers is called Helmholtz plane where diffusion of ions happen. After the Helmholtz plane towards electrolyte layer, there are also inner and outer Helmholtz layers. In general in the inner Helmholtz layer reactions are slower than outer Helmholtz layer. Ion intercalation and insertion processes happen in the inner layer. The potential difference that generates in the electrode interface is the double layer capacitance [18-23]. Therefore, at lower temperatures diffusion rate in the electrode interface was lower and accumulation of charged ions in the interface were also lower as seen at the lower temperature data. And at higher temperatures in the electrode interface, accumulation of lots of ion made capacitance value higher through the higher diffusion or intercalation rates.

CONCLUSION

The double layer capacitance in high capacity lithium-ion battery had been investigated. Experimental based results had been presented for a wide range of temperatures from -20 ºC to 50 ºC at various state of charge (SOC) conditions. It can be concluded from this experimental study that at lower temperatures, the cathode interfacial capacitance was lower and the state of the charges of the battery had a little effect on it. However, at high temperatures, the values of the double layer capacitance were much higher and it increased by 900% when the temperature was changed from -20 ºC to 50 ºC at the 50% SOC condition. The increases in the double layer capacitance values were higher for higher SOC conditions at the temperature changes considered in this study.

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