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Electrochemical Impedance Spectroscopy based voltage modeling of lithium Thionyl Chloride (Li\SOCl₂) primary battery at arbitrary discharge

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ABSTRACT

Primary batteries possess high energy densities that is beneficial to numerous important applications where recharging is impossible or impractical. The ability to accurately predict the voltage behavior of the battery under certain discharge regime is crucial in battery selection. In this work, Electrochemical Impedance Spectroscopy based approach is applied to predict the voltage of Lithium Thionyl Chloride (Li/SOCl₂) primary battery under two discharge conditions. The predicted voltage responses show high accuracy with minor deviations related to the passivation phenomena at the anode. Relevant corrections were made to improve the accuracy of the simulated voltages. The modeling method shows accurate voltage predictions at all states of charge. Moreover, the method was used to predict the voltage of Lithium Manganese Dioxide (Li/MnO₂) primary battery. The results show decent match with the experimental values demonstrating the applicability of the method to other chemistries of primary batteries.

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1. Introduction

Electrochemical Impedance Spectroscopy (EIS) has been employed to model the voltage behavior of various energy storage systems (ESS) [1–4]. EIS as an in-situ nondestructive technique provides rich information regarding the physical properties and the time constants of electrochemical phenomena [5,6]. The information obtained is implemented to predict the voltage behavior of the ESS under certain charge/discharge regimes. The applicability of the used method is determined by its accuracy and complexity [7–10].

Two main approaches are implemented in predicting the voltage behavior of ESS. The first is based on equivalent circuits (EC), in which electrochemical phenomena are represented by passive electric elements such as resistors and capacitors [8,11]. The second applies first principles models which depends on the thermodynamic and the kinetic properties of the system [12,13].

In EC modeling, the parameters are obtained by performing proper EC elements fit to the impedance data. Voltage behavior is then predicted using the parameters of the circuit obtained. This

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procedure is simple and straightforward; however, it lacks high accuracy and suffers from inconsistency and degeneracy in choosing the EC elements in the circuit [10,11]. On the other hand, first principles methods suffer from high complexity in obtaining the modeling parameters and may lead to over-parameterization which cause further difficulties [14,15].

In another approach by Ozdemir et al. [16], the voltage behavior of ESS under different discharge regimes can be predicted using EIS. In their modeling methodology, complex multiplication of the impedance with the current in the frequency domain is achieved to obtain the voltage. This methodology proved its applicability with high accuracy to predict the voltage behavior of secondary batteries and supercapacitors [16,17] and shows the potential to be used in modeling primary batteries.

Primary batteries possess higher volumetric and gravimetric energy densities than their secondary counterparts [18,19]. Among their different types and chemistries, Lithium Thionyl Chloride (Li\SOCl₂) is the most widely used. It has high energy density, high (~3.6 V) and very stable operating voltage through the discharge with large operating temperature range (-55 to 70 C) [20,21]. Applications such as, military, specialty emergency services and aerospace are heavily dependent on primary batteries [22,23].

Li\SOCl₂ battery composes of metallic Li foil anode and highly





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Fig. 1. EIS-based modeling methodology for predicting the voltage response of Li\SOCl₂ cell at arbitrary discharge. Input [1] is the EIS measurement of the cell, Input [2] is the arbitrary discharge profile. The Output is the time domain voltage response for the applied profile.

porous carbon cathode. The electrolyte is a solution of LiAlCl₄ (Lithium Aluminum Tetrachloride) dissolved in SOCl₂ (Thionyl Chloride) which is also used as the cathode active material [22]. During discharge, Li reacts with the electrolyte (SOCl₂) and electrons flow through the outer circuit. However, under open circuit conditions, Li continues to react with the liquid electrolyte causing the passivation of Li surface. This results in a dynamic process of formation and destruction of the Solid Electrolyte Interphase (SEI) every time the battery is discharged [24,25]. This phenomenon effects the voltage of the cell causing voltage delays at the start of the discharge and recovery after stopping the discharge of the battery [26–28].

Understanding the voltage behavior of Li\SOCl₂ battery under several discharge conditions is crucial for its correct implementation. In the literature, to the authors' knowledge, no EIS based modeling study was conducted to predict the voltage of primary batteries with Li\SOCl₂, nor any other chemistry. The reason may be related to the complications faced in performing EIS measurements for Li\SOCl₂ batteries. Modeling studies performed are one- and two-dimensional first principles in which the voltage behavior of the cell is predicted at constant discharge [29-31]. The number of free parameters in these models cast doubt on the validity of the approaches.

EIS measurements for Li\SOCl₂ batteries provide significant challenges. Excitation with perturbations around open circuit potential is not applicable since the chemistry is irreversible in which charge signals cause undefined reactions [32]. Moreover, the impedance of the passive layer at the anode dominates the cell's impedance. In a previous study [33], we introduced a solution to obtain linear and stable impedance data for Li\SOCl₂ by applying appropriate Direct Current (DC) offset along with Alternating Current (AC) excitation signal.

The current work demonstrates how the voltage of Li\SOCl₂ primary batteries can be predicted under different dynamic discharge regimes using EIS based model. The modeling methodology [16] does not utilize equivalent circuits, free of parameters and uses the impedance data as it is. We further improved the modeling methodology by doing the necessary corrections for the



Fig. 2. Environmental Protection Agency current profiles, Heavy Duty Urban Dynamometer Drive Schedule (HDUDDS) [Up] and Highway Fuel Economy Test Drive Schedule (HighwayFET) [Bottom], charging currents were replaced with zero currents to suit primary battery conditions.



Fig. 3. Bode and Nyquist plots for the EIS of Li\SOCl₂ at 85% SoC at the corresponding frequencies of the discharge current profile, Kramers-Kronig test is applied to check for the linearity and stability of the obtained data.

deviations caused by the formation and breakdown of the passive layer. These corrections are required for lithium anodes used in the primary batteries as compared to the alloys used in the secondary batteries. Additionally, we studied the voltage response of the cell at different states of charge. Finally, the method was used to predict the voltage behavior of Lithium Manganese Dioxide (Li\MnO₂) primary batteries to show the applicability of the method to other chemistries.



Fig. 4. Calculated and measured voltage responses (Up) and percent proportional voltage error for the calculated voltage response (Bottom) of the Li\SOCl₂ cell plus –50mA DC-offset for HDUDDS.



Fig. 5. Calculated and measured voltage responses (Up) and percent proportional voltage error for the calculated voltage response (Bottom) of the Li\SOCl₂ cell plus –50mA DC-offset for HighwayFET.

2. Methods

2.1. - Cells

Commercially available Li/SOCl₂ (SAFT-LSH20) D-size spiral cells were used in all the measurements. The cell has 13Ah capacity with 3.67 V open circuit potential. For Li/MnO₂ batteries (Maxell CR2032) coin cell was used with 220 mAh and 3.0 V open circuit potential.

2.2. - EIS measurements

EIS measurements were done in a galvanostatic mode at discharge. Direct Current (DC) is applied along with the Alternating Current (AC) excitation signal as shown in Fig. 1 (Input [1]). Gamry Interface 1000E potentiostat/galvanostat/ZRA was used for obtaining the EIS data. In all EIS measurements, -50 mA DC offset was used along with 5 mA AC as the excitation signal. The measurement script was adjusted to measure the impedance at the required frequencies. The frequency window was linearly spaced between 0.5 Hz and 940 µHz which was obtained from the FFT output of the current profiles. The first frequency in the window is half of the sampling rate (1 s) and the last is the inverse of the length of the profile. The total time for EIS measurement was 26,316 s. For the state of charge (SoC) experiments, each EIS measurement discharged the cell by 2.7% of the nominal capacity. The cell was discharged with -100mA between the EIS measurements in a controlled manner. This allowed for the investigation of the EIS until 30% SoC in which cutoff frequency was reached.

2.3. - Modeling methodology

The modeling methodology is based on the Zero-Free Parameter method published by Ozdemir et al. [16], and the steps of the process are shown in Fig. 1. In the process, the first step after obtaining the EIS (Input [1]) of the cell is to Fast Fourier transform (FFT) the current profile (Input [2]). The second step is to multiply the impedance values by the current values at every frequency of interest. This result, according to Ohm's law, in the voltage response of the cell at the frequency domain. Inverse-FFT is performed to the frequency domain voltage response to obtain the time domain voltage response of the cell. Finally, correction of the voltage response for the voltage recovery caused by the passivation reaction is done to obtain the accurate voltage response. This last step was not performed in the rechargeable batteries that Ozdemir et al. [16]. had studied.

2.4. - Current profiles

Current profiles were chosen from the published Environmental Protection Agency (EPA) profiles [34]. The first is Heavy Duty Urban Dynamometer Drive Schedule (HDUDDS) and the second is Highway Fuel Economy Test Drive Schedule (HighwayFET). These profiles are published as arrays of speeds in time domain. Obtaining the time domain current profile from the speed time domain profile was done by calculating the local accelerations as simple two-point finite differences. Accelerations were normalized to have the highest acceleration level to be unity. The power is assumed to be directly proportional to the current drawn from the batteries. Because this study explicitly employs primary batteries, charging currents were replaced with zeros. The maximum discharge current amplitude was adjusted to -500mA as shown in Fig. 2. In the initial modeling results, a DC-offset was applied along the current profiles to prevent the cell from falling into voltage recovery behavior caused by the passivation of the anode at open circuit.



Fig. 6. Calculated and measured voltage responses (Up) and percent proportional voltage error for the calculated voltage response (Bottom) of the Li\SOCl₂ cell for HDUDDS.

After that the profiles were applied without the DC-offset where passivation reaction caused voltage recovery behavior at open circuit potential. The experimental voltage response for the current profiles were recorded by Gamry Interface 1000E potentiostat/ galvanostat/ZRA using adjusted measurement script.



Fig. 7. Calculated and measured voltage responses (Up) and percent proportional voltage error for the calculated voltage response (Bottom) of the Li\SOCl₂ cell for HighwayFET.

2.5. - Voltage recovery treatment

The recovery treatment was performed by first recording the voltage response of the cell at different discharge currents followed by open circuit potential for calibration. The voltage recovery curves obtained from these voltage responses were averaged to one curve and then normalized. The curve was fitted to a mathematical function using scipy. optimize.curve_fit script [35] in Spyder 3.3.3, which could predict the voltage recovery behavior as a function of time. The parametrized function was used to calculate the required voltage recovery correction in the last step in the modeling procedure which corrects for the voltage response at zero currents.

3. Results and discussion

3.1. - Impedance results

The result of the galvanostatic EIS at discharge for the Li\SOCl₂ linearly spaced frequencies between 0.5 Hz and 940 µHz are shown in Fig. 3. Kramers-Kronig (KK) test was applied as shown to check for the linearity and the stability of the obtained spectrum. The KK compatibility was tested using Gamry Analyst software which use linear measurement model approach developed by Boukamp [36].

(a)

As can be seen the data is compatible with the KK transform which indicates the linearity and stability of the data. The Bode plot contains the absolute impedance values and the phase angle vs. the frequency.

3.2. - Voltage response at DC-offset

The calculated and the experimentally measured voltage response of the Li\SOCl₂ to the HDUDDS and HighwayFET current profiles with the DC offset are shown in Figs. 4 and 5 respectively. The starting voltage is around 3.55 V due to the applied DC offset which was applied to minimize the voltage recovery behavior at open circuit. There is a good overlay between the calculated and the experimentally measured values. The proportional errors for both profiles which are shown in Figs. 4 and 5 (bottom) are less than 1.00% for both profiles.

3.3. - Voltage response at open circuit potential (OCP)

The voltage response at OCP results in higher proportional errors which can be seen in the overlay of the calculated and the experimental voltages shown in Fig. 6 and 7. As can be seen, the simulated voltages deviate from the experimental ones at zero



Fig. 8. Voltage response of Li\SOCl₂ at (a) OCP + constant discharge currents followed by zero current, (b) fitting curve for the averaged and normalized voltage recovery response.

current segments which is related to the voltage recovery caused by the passivation reaction. During zero current (recovery), the calculated voltage stays roughly constant at a certain voltage while the measured increases with time. This deviation at the zero currents can be corrected by the method developed in the current manuscript which adjusts the voltage response specifically at these regions based on the voltage calculated from the calibration data.

3.4. - Voltage recovery treatment

The deviations in the calculated voltage response from the experimental measurements due to the formation of the passivation layer (voltage recovery) can be minimized by adjusting the voltage response at those regions. The behavior of the voltage recovery at (OCP) after discharge by different currents are shown in Fig. 8(a). This measured voltage recovery behavior was averaged and normalized as to give a general behavior with one curve which is shown in Fig. 8 (b). This curve was fitted with a mathematical function shown below, which predicts the normalized voltage response as a function of time:

$$V(t) = a\sqrt{t} + be^{-ct} + d$$

where, a = 0.065, b = -0.502, c = 0.176 and d = 0.500.

This function was chosen with a generic diffusion and a capacitive relaxation in mind. Using a square root of time to model a generic diffusion response and a single-exponential relaxation function to model a capacitive decay. The ultimate details of the recovery process are more detailed and beyond the scope of the current study. This function was used to correct for the voltage response at the regions of zero current.

The corrections in the voltage response at the voltage recovery regions resulted in a better agreement with the experimentally measured voltage response. The corrected voltage responses are shown in Figs. 9 and 10 along with the uncorrected and the experimentally measured ones. The proportional error graphs demonstrate a decrease in the error levels particularly at zero current regions where voltage recovery exists.

3.5. - Voltage modeling at different states of charge

Investigation of the voltage response of the Li\SOCl₂ battery at different states of charge (SoC) was done by applying the same method for fully charged battery and with levels of discharged batteries until 30% SoC. The Nyquist plots of the EIS at different SoC are shown in Fig. 11. The distorted semicircle shows itself at all the SoC with small shifts in the transition frequency. The impedance spectrum at the high and the low SoC in Fig. 11 show deviations in the KK compatibility test which indicates the presence of instabilities or nonlinearities. At high SoC the deviations are caused by the intense passivation reaction due to the high amount in electrolyte (SOCl₂) which decreases by discharge. On the other hand, at the low SoC voltage instability causes the deviations. The rest of the impedance data in Fig. 11 show better compatibility with the KK indicating the stability and the linearity of the obtained EIS.

The calculated and the experimentally measured voltage responses for the two profiles are shown in Fig. 12. There is good overlap for the calculated and the measured voltage profiles at all SoC as can be also seen from the proportional error profiles shown in Fig. 13. The deviations in the impedance data from the KKtransforms at high and low SoC reflect themselves in the voltage responses as can be seen in the voltage profiles and the proportional error at 100, 95 and 35 %SoC shown in Figs. 12 and 13. However, the rest SoC data show better voltage responses with lower proportional errors.



Fig. 9. Calculated and measured voltage responses (Up) and percent proportional voltage error for the calculated voltage response (Bottom) after applying recovery correction for HDUDDS.

3.6. - Application to another primary battery chemistry (Li/MnO₂)

To demonstrate the applicability of the used modeling methodology in predicting the voltage behavior of other primary batteries, Lithium Manganese Dioxide (Li/MnO₂) primary coin



Fig. 10. Calculated and measured voltage responses (Up) and percent proportional voltage error for the calculated voltage response (Bottom) after applying recovery correction for HighwayFET.



Fig. 11. Nyquist plots for the EIS of Li\SOCl₂ battery from 100% to 30% states of charge.



Fig. 12. Calculated and experimentally measured voltage responses at different SOC for (a)HDUDDS and (b) HighwayFET.



Fig. 13. Percent proportional voltage error for (a)HDUDDS and (b) HighwayFET at different SoC.



Fig. 14. Calculated and Measured voltage response of Li/MnO₂ primary battery under a) HDUDDS and (b) HighwayFET discharge profiles. Proportional voltage error for c) HDUDDS and d) HighwayFET.

batteries were used. The same procedure was applied with the current profiles maximum amplitude adjusted to -10mA to account for change in capacity. The results are shown in Fig. 14 in which decent overlap between the experimentally measured and the calculated voltage with less than 0.3% proportional error are observed.

4. Conclusion

EIS based modeling methodology was presented to predict the voltage behavior of the Li\SOCl₂ under arbitrary discharge. The modeling methodology showed accurate results for predicting the voltage response with less than 1% proportional errors. The small deviations are due to the passivation layer continuous formation and destruction at the surface of the anode Li. We minimized the deviations by calibrating the behavior of the voltage under the passivation effect and correcting the voltage response according to mathematical fits. Investigation of the voltage response at different SoC was also achieved. Higher errors were observed at the 100-95% SoC due to the deviations in the impedance results caused by the strong passivation. However, the response was accurate for the rest of the SoC with less than 1% proportional error. Finally, the method was applied to Li/MnO₂ primary battery which predicted the voltage response with less than 0.3% proportional error. This shows the applicability of the modeling methodology to predict the voltage behavior of primary batteries at arbitrary discharge regimes.

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