IDENTIFICATION OF DIFFERENTIAL CAPACITY IN LITHIUM-ION BATTERIES BY DECONVOLUTION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT

Electrochemical impedance spectroscopy (EIS) allows detailed investigations of polarization processes and is widely used to study the kinetics of electrode reaction in lithium-ion batteries. The distribution of relaxation times (DRT) calculated from the EIS offers a model-free approach for a deeper understanding of various electrochemical processes. A joint estimation method is proposed to identify the differential capacity caused by diffusion processes and the DRT for all polarization processes simultaneously. The differential capacity from EIS and the incremental capacity from incremental capacity analysis (ICA) have an equivalence verified by mathematical derivation. Different types of lithium-ion batteries are tested by the EIS and the ICA methods to verify the equivalence. The differential capacity extends the application of the ICA method.

Keywords: electrochemical impedance spectroscopy, distribution of relaxation times, differential capacity, joint estimation method

1. INTRODUCTION

Electrochemical impedance spectroscopy (EIS) has proven to be a powerful tool for investigation of complex electrochemical systems including lithium-ion batteries, fuel cells and has been widely used to characterize the polarization processes at different scales in lithium-ion batteries [1]. EIS is usually analyzed by a carefully chosen equivalent circuit model (ECM), which requires knowledge about the electrochemical processes at each electrode within the cell. However, the non-ideal processes and the overlapping effects lead to the ambiguity of the ECM. This problem can be settled by a deconvolution of the EIS with the distribution of relaxation times (DRT). DRT offers a model-free approach without the need for any prior knowledge of the investigated electrochemical system and has been successfully applied to decompose the EIS of solid oxide fuel cells (SOFC) [2]. For lithium-ion batteries, the

NOMENCLATURE

Abbreviations	
DDC	distribution function of differential capacity
DIA	differential impedance analysis
DRT	distribution of relaxation times
ECM	equivalent circuit model
EIS	electrochemical impedance spectroscopy
ICA	incremental capacity analysis
SOFC	solid oxide fuel cells

Symbols	
$\mathbf{A'}$	approximation matrix of the DRT for the real part of the EIS
$\mathbf{A''}$	approximation matrix of the DRT for the imaginary part of the EIS
C_{diff}	differential capacity
$I(\omega)$	battery current in the frequency domain
$J(\mathbf{x})$	Sum of squares with respect to $\mathbf{x}$
n	Number of samples for EIS measurement
R_{ohm}	ohmic resistance
$U(\omega)$	battery voltage in the frequency domain
$\mathbf{x}$	vector of the parameter for DRT approximation
$\mathbf{Z'}_{exp}$	impedance vector of the real part
$\mathbf{Z''}_{exp}$	impedance vector of the imaginary part
ω	frequency

differential capacity at low frequencies has to be considered as shown in Fig. 1, and thus, the DRT needs to be modified as the DRT does not include pure capacitive behavior. Some methods have been proposed to estimate the differential capacity, such as preprocessing method [3], distribution function of differential capacity (DDC) method [4] and differential impedance analysis (DIA) method [5]. However, the differential capacity and the DRT are estimated separately, resulting in accumulation of errors and limiting the application of DRT in lithium-ion batteries.

In this paper, a joint estimation method is proposed to identify the differential capacity (C_{diff}) and the DRT simultaneously to minimize errors and obtain more information about diffusion processes from EIS.
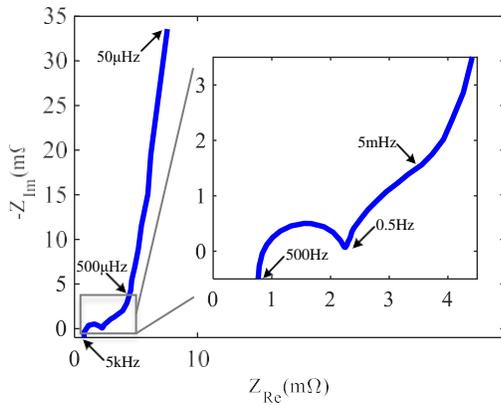
Fig 1 EIS of a lithium-ion battery with capacitive tail, measured from 5kHz to 50µHz

2. METHOD

2.1 The relationship between EIS and ICA

In this section, a derivation is provided to explain the relationship between the differential capacity C_{diff} from EIS and incremental capacity from ICA.

A typical EIS involves sweeping the excitation frequency with sinusoidal excitation. For the EIS, the impedance can be described by a frequency dependent function:

$$Z(\omega) = \frac{U(\omega)}{I(\omega)} = R_{\text{pol}} + \frac{1}{j\omega C_{\text{diff}}} \qquad (1)$$

The differential capacity C_{diff} can be separated by finding the limit at low frequencies,

$$C_{\text{diff}} = \lim_{\omega \to 0} \frac{\frac{j\omega}{}}{\frac{U(\omega)}{I(\omega)} - R_{\text{pol}}} = \lim_{\omega \to 0} \frac{j\omega I(\omega)}{U(\omega)} = \lim_{\omega \to 0} \frac{Q(\omega)}{U(\omega)} = \frac{dQ}{dU} \quad (2)$$

The equivalence between the differential capacity C_{diff} and the incremental capacity can be proved from Eqn. (2). Graphical visualization of the relationship between the differential capacity C_{diff} from EIS and incremental capacity from ICA is given in Fig. 2 for a better understanding of the equivalence.
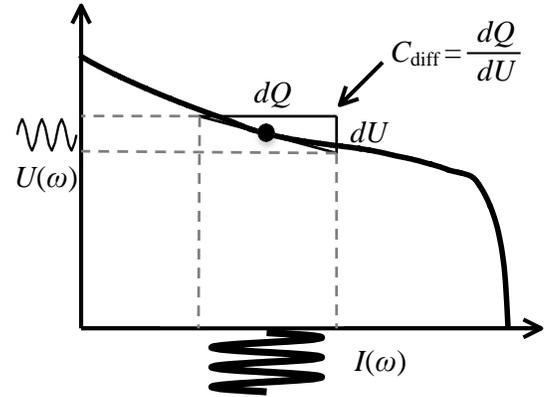
Fig 2 Relationship between the differential capacity from EIS and incremental capacity from ICA

2.2 Derivation of the joint estimation method

The impedance model given in Ref. [6] can be transformed into Eqn. (3) considering the capacitive properties at low frequencies,

$$Z(\omega) = R_{\text{ohm}} + (\mathbf{A'x})_n + (\mathbf{A'x})_n + \frac{1}{j\omega C_{\text{diff}}} \qquad (3)$$

then the joint estimation function can be obtained by fitting the impedance model $Z(\omega)$, which implies the minimization of the following sum of squares:

$$J(\mathbf{x}) = \left\| \mathbf{\Omega'}\left(R_{\text{ohm}}\mathbf{1} + \mathbf{A'x} - \mathbf{Z'_{\text{exp}}} \right) \right\|^2 +$$
$$\left\| \mathbf{\Omega''}\left(\frac{1}{2\pi\boldsymbol{\omega}C_{\text{diff}}} + \mathbf{A'x} - \mathbf{Z''_{\text{exp}}} \right) \right\|^2$$

where $\mathbf{1}$ is a column vector with n entries all equal to 1, $\boldsymbol{\omega}$ is a column vector equal to the sweeping frequency.

3. EXPERIMENT

3.1 The test batteries

Fig. 3 shows the batteries used for tests, and Table 1 lists the specifications. The batteries are assigned with capital characters A, B, and C for the convenience of further discussion. Two of the batteries have cathodes with $LiNi_xCo_yMn_zO_2$ (NCM), and the other has a mixed cathode material with NCM and $LiMn_2O_4$ (LMO). All batteries have anodes with graphite.

3.2 The test profiles

Two test profiles were established. The profile to test the EIS is described in Table 2, and the profile to test the ICA is described in Table 3.

As shown in Fig. 4, the battery test bench consists of a Neware CT-4008-5V100A-NTFA tester, a thermal chamber for ambient temperature, an Autolab PGSTAT302N electrochemical workstation for EIS test, and a host computer. The Neware tester is used to charge and discharge the batteries, and its sampling frequency is 1Hz. EIS tests were obtained at every 10% SOC interval from 100% SOC to 0% SOC. The applied voltage amplitude is 5mV, and the frequency range in 2kHz – 2mHz (60 points).

Fig 3 Batteries used in the experiments

4. RESULTS AND DISCUSSIONS

In this section, the identification results using the joint estimation method are provided, and the comparison of the differential capacity C_{diff} and the incremental capacity is conducted.

4.1 The EIS results

Fig. 5 shows the EIS of Cell A, Cell B and Cell C, respectively. The EIS results are shifted in y-direction for better visualization.

4.2 The identification results of differential capacity C_{diff}

Fig. 6 shows the identification results of C_{diff} in the red cross and the ICA curves in the blue line. It can be seen that each identification result is close to the ICA value of the corresponding voltage. The relative errors are shown in Fig. 7, indicating the high accuracy of the method.
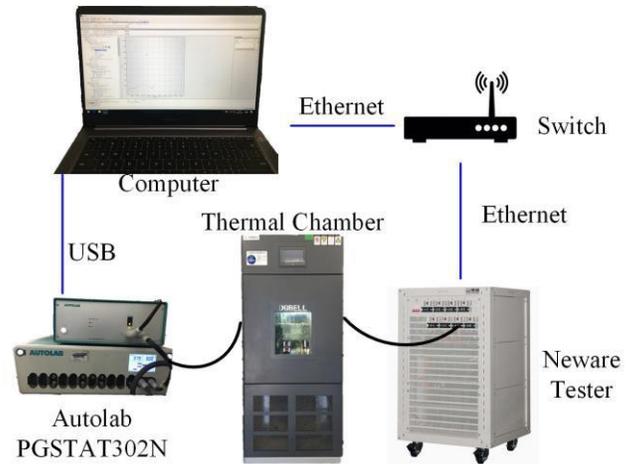
Fig 4 Battery test bench

Table 1 specifications of the batteries

Battery	Cathode	Anode	Rated Capacity (Ah)	Voltage range (V)
A	NCM	Graphite	3.2	2.5-4.2
B	NCM	Graphite	4.8	2.5-4.2
C	NCM+LMO	Graphite	24	2.5-4.2
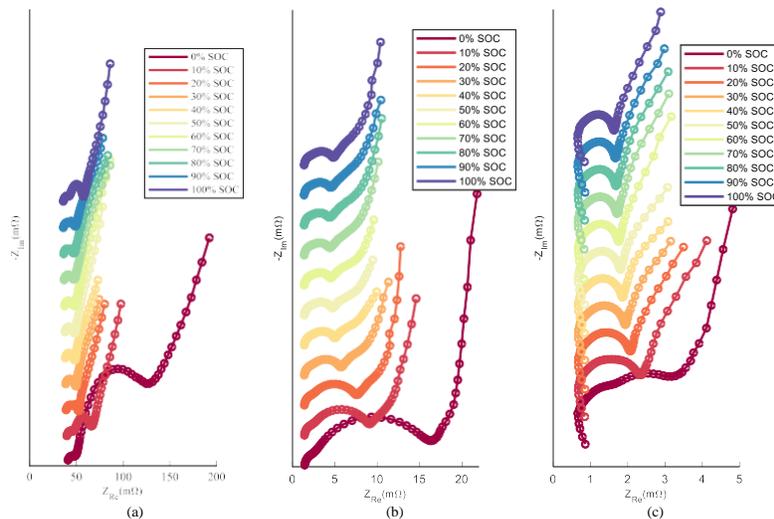
Fig 5 EIS results with (a) Cell A, (b) Cell B, (c) Cell C
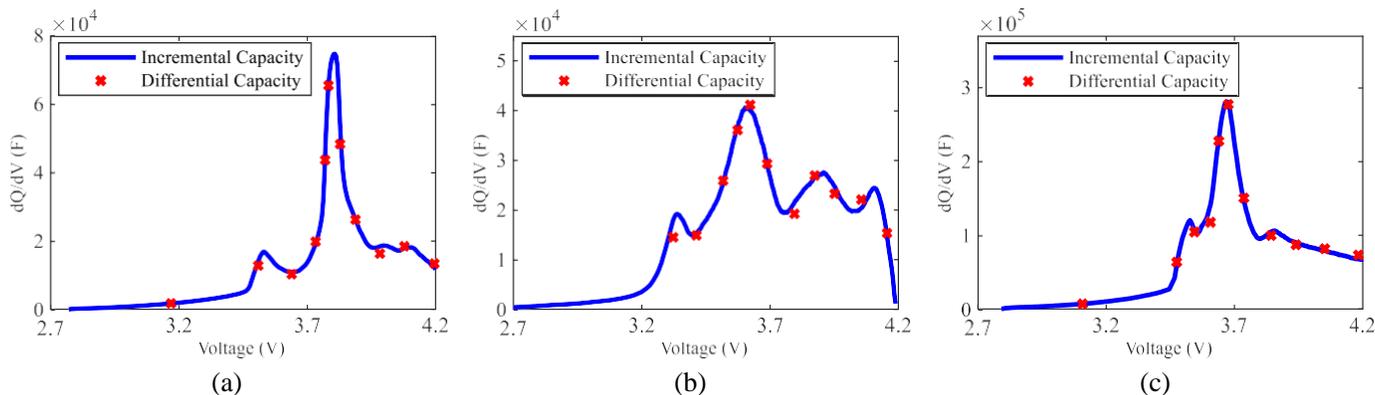
Fig 6 Identification results of differential capacity C_{diff} compared with ICA

Table 2 Test profile 1 for EIS measurements

Step no.	Step name	Duration	Current	Cycle no.
1	Rest	180 min		
2	EIS test			
3	Discharge	18 min	1/3 C	
4	Cycle, step 1-3			10
5	Rest	180 min		
6	EIS test			
7	End			

Table 3 Test profile 2 for ICA measurements

Step no.	Step name	Duration	Condition	Cycle no.
1	Rest	180 min		
2	Discharge		$I = 1/3$ C	
3	Rest	180 min		
4	Charge		$I = 1/3$ C	
5	Constant voltage charge		$V =$ upper limit	
6	Cycle, step 1-5			3
7	Rest	180 min		
8	Discharge		$I = 1/20$ C	
9	Rest	180 min		
10	Charge		$I = 1/20$ C	
11	End			
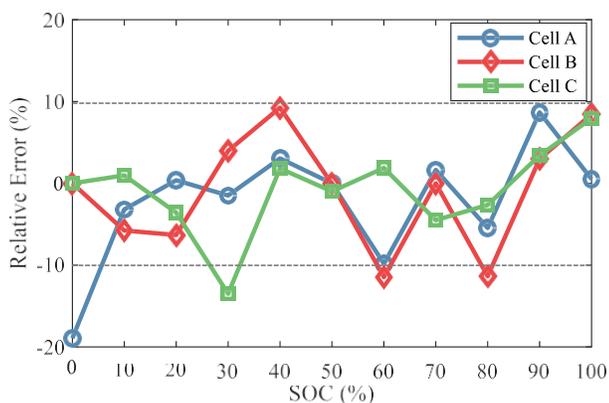
Fig 7 Relative errors

5. CONCLUSION

This paper introduces a joint estimation method to identify the differential capacity C_{diff} from the EIS data of lithium-ion batteries. The verification of the equivalent basis of the differential capacity C_{diff} and the incremental capacity is derived. Also, different types of lithium-ion batteries are employed to test the joint estimation method. Actual data shows that the identification results are consistent with the incremental capacity value of ICA. The proposed joint estimation method can provide an intuitive understanding of the capacitive characteristics in lithium-ion batteries and has the potential for SOH evaluation based on the interpretation of the ICA.

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