Li-ion Battery Charge Transfer Stability Studies with Direct Current Impedance Spectroscopy

Yun Bao* and Yinchu Gong

Department of Applied Physics, Donghua University, China

E-mail address: bao_yun@dhu.edu.cn

Introduction

- The safety of lithium-ion batteries is closely related to the charge transfer process inside the battery. Due to technical limitations, the current battery thermal failure management system cannot realize risk early warning.
- Due to the high cost of test equipment and high signal-to-noise ratio requirements, electrochemical impedance spectroscopy (EIS) is still not applicable to electric vehicles.
- In addition, R_{ct} is affected by ambient temperature and battery aging, which brings challenges to online safety diagnosis.
- Here we propose a method to obtain the activation energy of a battery using DC impedance spectroscopy (DCIS), which enables the stability diagnosis of the charge transport process.

Charge and Discharge of Lithium Batteries

- Step1. The solvation/de-solvation process of Li-ions at the SEI/electrolyte interface.
  Step2. The Li-ion transport process in the SEI.
  Step3. The intercalation/de-intercalation process of li-ions at the SEI/electrode interface.
- The electrochemical model represents the electrode/electrolyte interface with a resistive-capacitive (RC) network composed of R_{ct} and double-layer capacitance (C_{dl}).
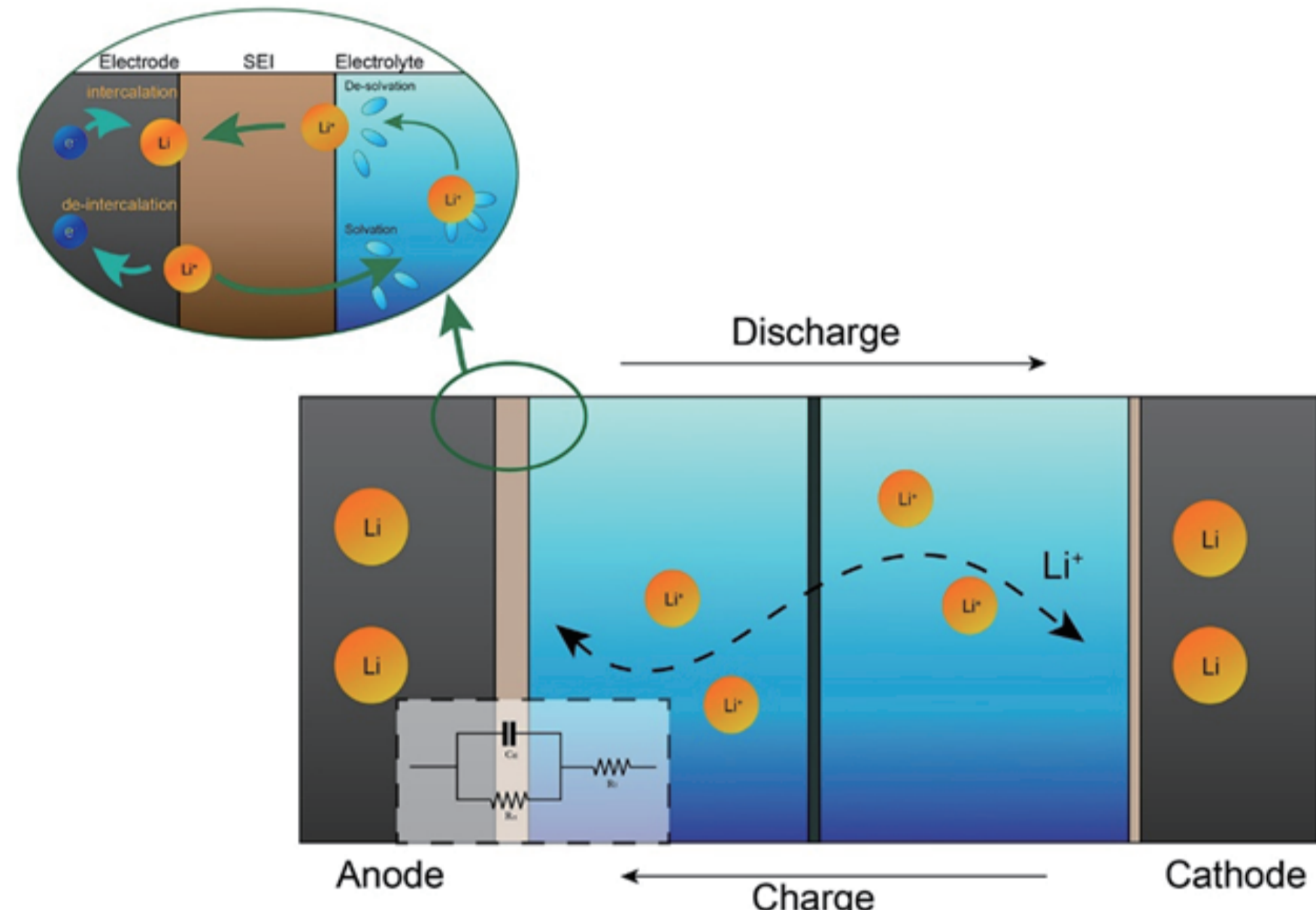

Fig. 1. Lithium-ion battery structure and equivalent.

DCIS

- Due to the frequency characteristics of the RC network, the impedance value of the lithium-ion battery can be expressed as below:

$$Z(\omega) = R_0 + \frac{1}{j\omega C_{dl} + \frac{1}{R_{ct}}} = R_0 + \frac{R_{ct}}{j\omega\tau + 1}$$

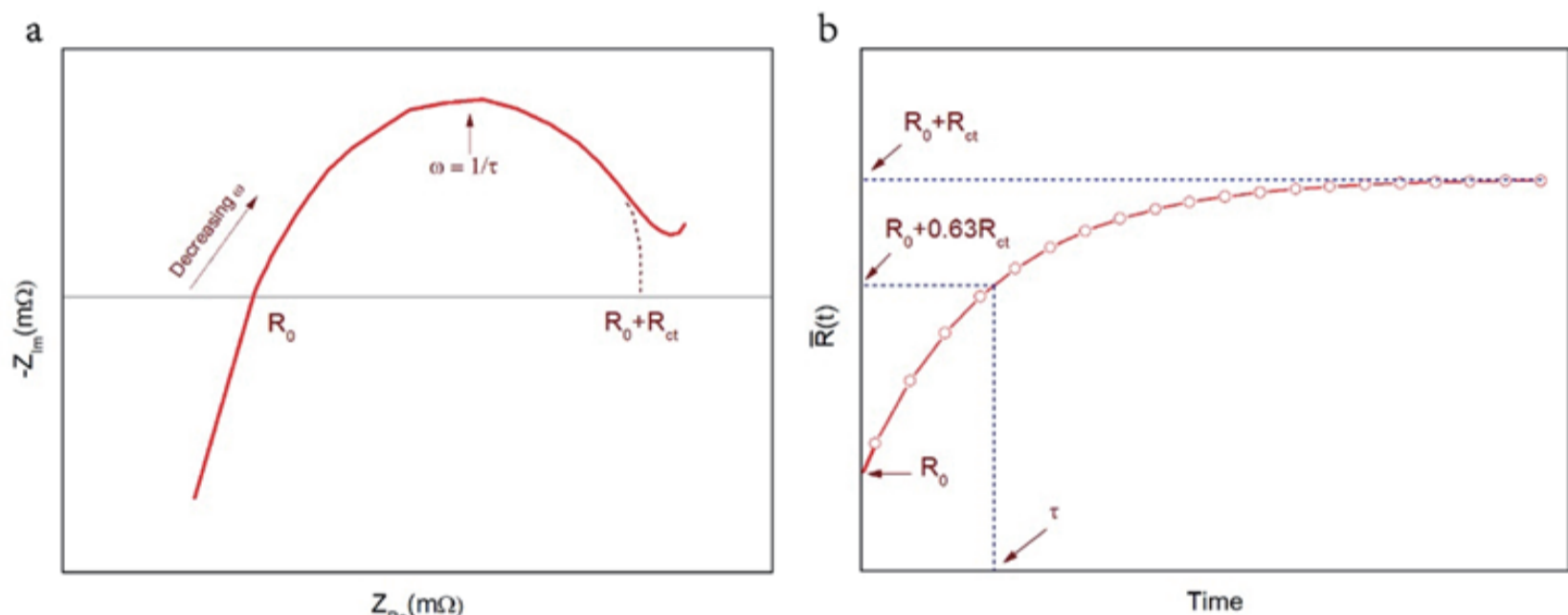The Nyquist plot in Fig. 2a is a frequency domain space EIS curve.

Fig. 2. Schematic diagram of (a) EIS; (b) DCIS.

- DCIS is a time-domain impedance spectroscopy technique. It uses the time constant characteristic of the internal RC network to detect battery parameters.
- Due to the RC network, the equivalent resistance of the battery is a function of time and can be expressed as follow:

$$\overline{R}(t) = \frac{\Delta V(t)}{I} = R_0 + R_{ct}\left(1 - e^{-\frac{t}{\tau}}\right)$$

Here τ is the time constant of the RC network. By changing the discharge pulse width, DCIS can obtain R_{ct} in the time domain using the time function of the equivalent resistance, as shown in Figure 2b.

Activation Energy

- As the charge transport process of lithium-ions is related to its diffusivity, the diffusion coefficient follows the Arrhenius equation.

$$\frac{1}{R_{ct}} = A exp\left(-\frac{E_a}{RT}\right)$$

- Activation energy (E_a) is an important indicator of the diffusivity of lithium-ions, and the diffusion coefficient decays exponentially with the increase of the energy barrier. In addition, as a microscopic parameter, the energy barrier of the electrode/electrolyte interface is not affected by temperature, which is beneficial for battery safety diagnosis in variable temperature environments.

Experiments and Results

- The experiment used the same batch of commercial 18650 lithium-ion batteries as the investigation samples.The room temperature internal resistance, capacity and SOH of the experimental battery samples are shown in Table 1.

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* Corresponding author.

Table 1. Internal resistance (IR), capacity and SOH of the battery samples.(Measured at room temperature)

Battery Sample	IR(mΩ)	Capacity(Ah)	SOH
cell 1	37.5	3.2	100%
cell 2	40.9	2.92	91.25%
cell 3	42.2	2.75	85.94%
cell 4	46.4	2.61	81.56%
cell 5	53.7	2.5	78.13%
cell 6	55.8	2.48	77.50%

- Figure 3 shows the DCIS of each sample cell. For the same cell, the DCIS curves are significantly different as the temperature changes, which indicates the R_{ct} temperature characteristics. As the temperature increases, the change in the DCIS curve becomes smaller, which means that the R_{ct} value decreases. The reason for the decrease in R_{ct} is that the diffusivity of lithium-ions increases at higher temperature.
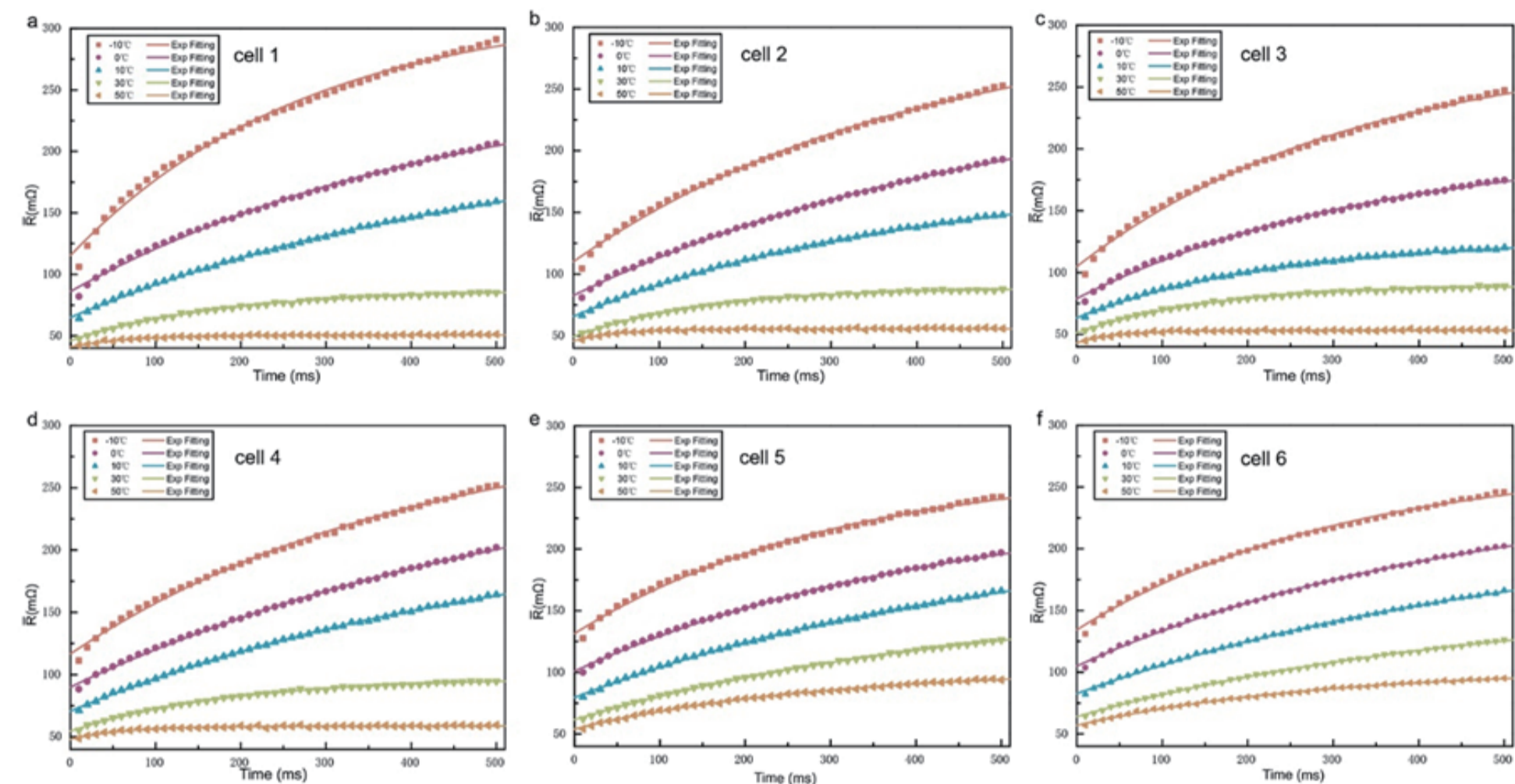

Fig. 3. Multi-temperature DCIS of aged battery samples.

- Further research shows that there is an exponential relationship between R_{ct} and temperature, as shown in Figure 4. This result is consistent with the Arrhenius equation. The activation energy of the battery sample can be obtained by exponential fitting.
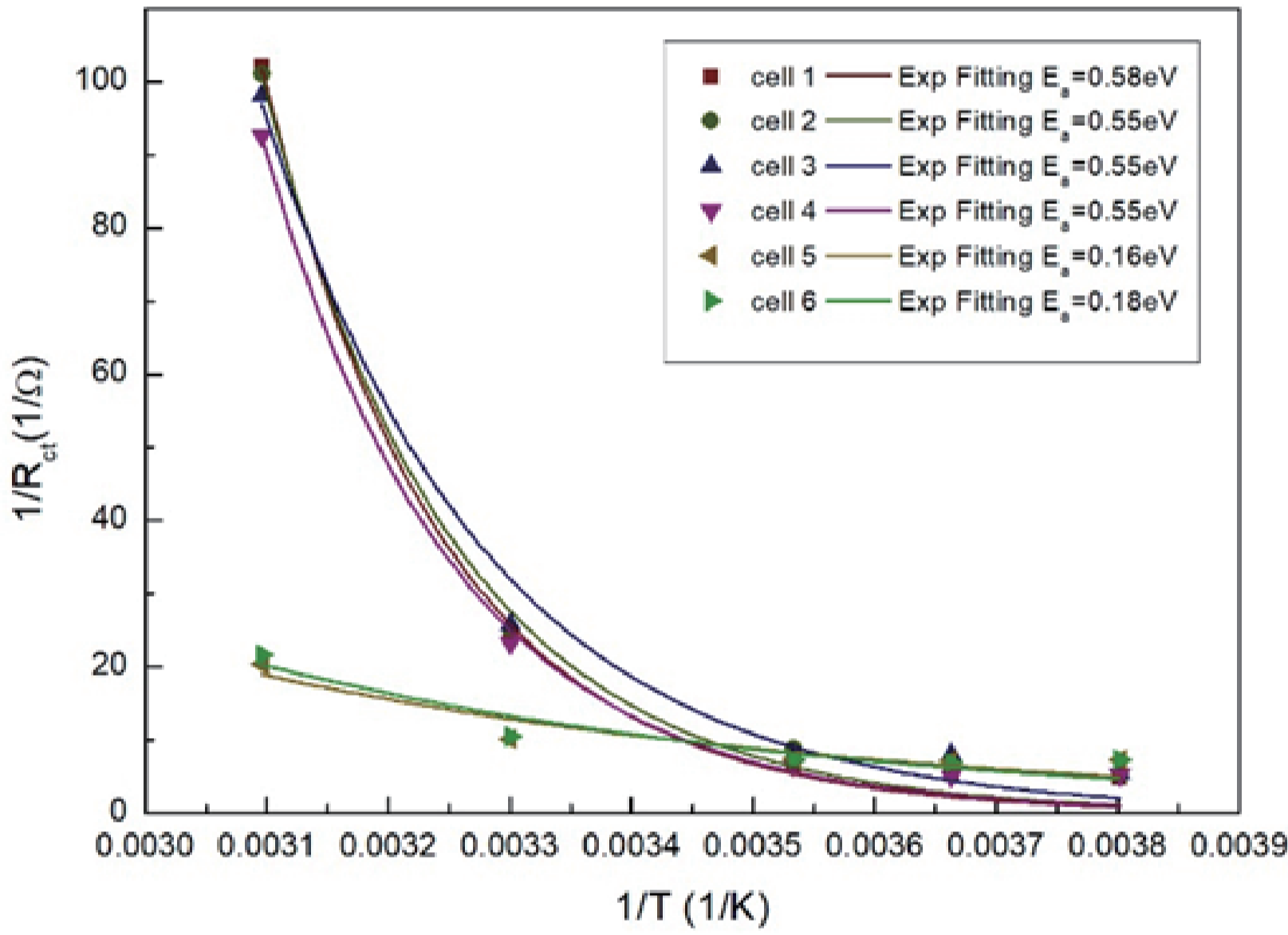

Fig. 4. Variation of R_{ct} with temperature.

- As shown in Figure 5, the SOH of samples 1-4 are all greater than 80%, which is a reasonable and healthy working state of lithium-ion batteries. The SOH of both samples 5 and 6 is less than 80%, and the E_a value drops significantly at this time, indicating that the excessive aging of the battery has begun to affect the electrode/electrolyte interface state.
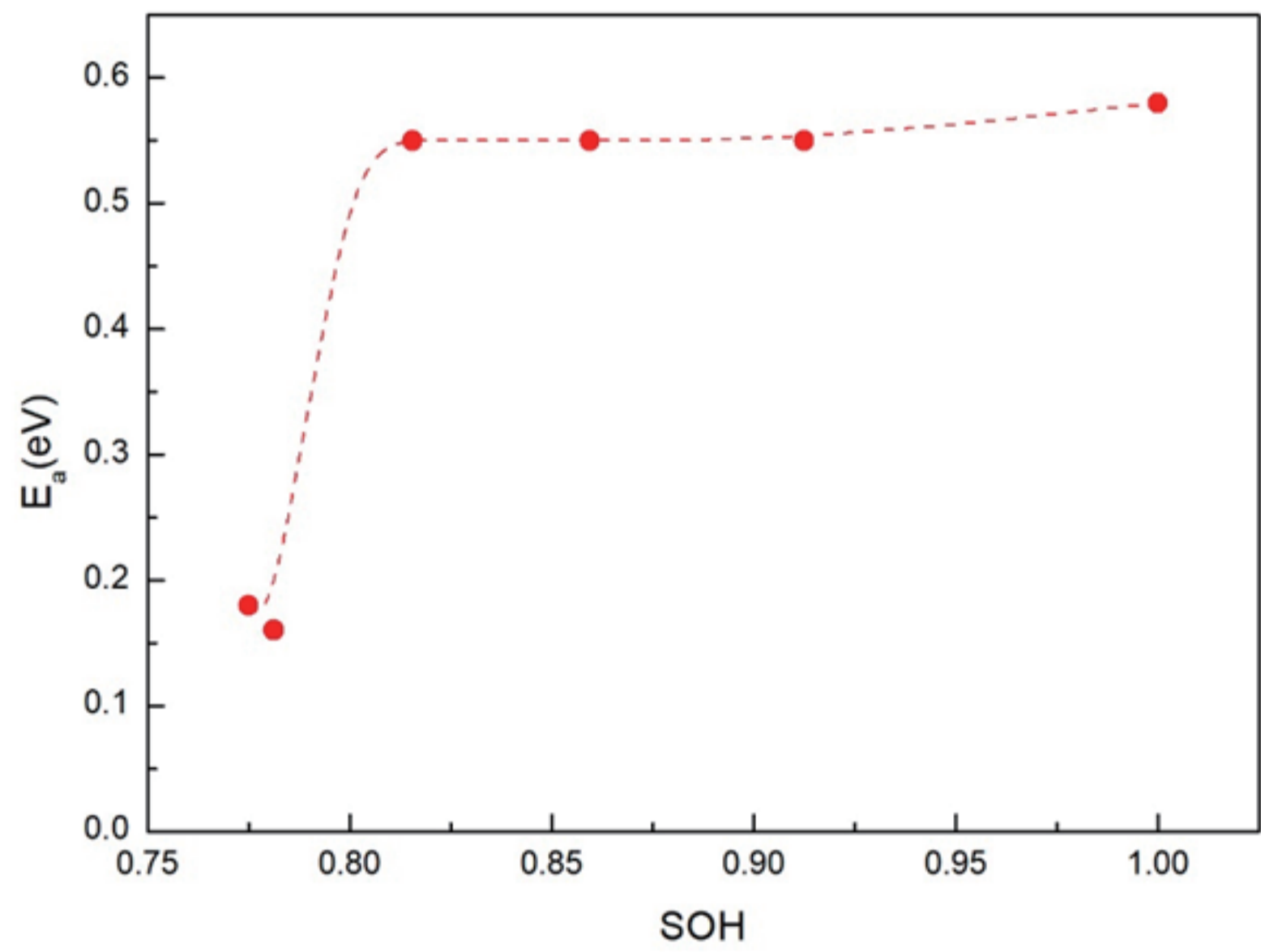

Fig. 5. Activation energy vs. SOH.

- In addition, the SOH of samples 1-4 covers the range of 80%-100% of the battery, and their activation energy is basically stable at 0.55eV, which indicates that the activation energy is not affected by the aging degree of the battery during normal use. However, when the battery life exceeds a critical value, the activation energy will drop rapidly, and the battery will face a serious risk of thermal runaway.
- In summary, the activation energy obtained by DCIS can directly diagnose the state of charge transport at the electrode/electrolyte interface and improve the battery safety management capability.

Summary

- Activation energy is the energy barrier for lithium-ions to cross the electrode/electrolyte interface and can indicate the stability of the charge transport process. Since activation energy is a microscopic parameter, it is not affected by temperature and aging, which is beneficial for battery safety diagnosis.
- DC impedance spectroscopy (DCIS) enables the stability diagnosis of the charge transport process by obtaining the activation energy of a battery.Since DCIS supports online detection, it provides an option for safety diagnosis of electric vehicle batteries.

Acknowledgements