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Impedance Characteristics and Diagnoses of Automotive Lithium-Ion Batteries at 7.5% to 93.0% State of Charge

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ABSTRACT

Diffusion behaviors and reaction kinetics are factors limiting the rate capacity of lithium ion batteries (LIB), particularly in automotive applications. In order to gain a better understanding of the rate-limiting factors of LIBS, a fractional circuit model is constructed and two feedback loops are added to the impedance diagnosis flowchart in this paper. The fractional impedance model is constructed for a commercially available automotive LIB, featured by low internal resistance, long diffusion lengths, and large interfacial areas. Impedance data collected are then used to quantitatively analyze the charge transfer reaction, the status of the solid electrolyte layer (SEI), and the lithium diffusion behavior at different state of charges (SOCs) of 7.5%$\sim$93.0% based on the constructed model and the calculated characteristics frequencies of the corresponding physiochemical processes. The results indicate that both charge transfer resistance and diffusion resistance increased dramatically with decreased SOC values when SOC $\leq$ 26.5%. These results suggest that automotive LIBs should not operate at low SOCs of less than 20.0% or depth of discharging higher than 80.0%. Finally, calculations of anode and cathode Warburg impedance percentages offer a simple and quick way to evaluate lithium diffusion abilities through insertion/de-insertion electrodes.

1. Introduction

Recently, Lithium-ion battery (LIB) technologies are experiencing rapid growth in a number of application areas including portable electronics, stationary power stations and electronic vehicles due to advantages such as salient operation, high energy density, high power density, long cycle-life and environmental friendliness [1,2]. For automotive applications, high capacity and high power LIBs are normally assembled into modules/packages for high-rate operations. Therefore, high-rate capabilities are a prerequisite for LIBs in electric vehicle (EV) applications. The rate capability of LIBs is profoundly dependent on the status of the solid electrolyte interphase (SEI), the insertion/de-insertion reaction and the diffusion behavior [3]. As for the battery management system (BMS) in EV applications, before LIBs are packed into electric vehicles, a quick and substantial diagnosis is required to ensure qualified performance. This is achieved through the testing of fundamental parameters such as direct current resistance, diffusion behavior, charge transfer reaction, and SEI status [4]. Moreover, above three factors of LIBs are all dependent of state of charge (SOC), so do ultracapacitors [5].

Electrochemical impedance spectroscopy (EIS or AC impedance) is a viable approach that can be used not only in LIBs [6] but also in other electrochemical energy storage and conversion devices, such as fuel cells [7] and ultracapacitors [5,8]. This is due to two main advantages [9,10]: (i) a small signal perturbation guarantees that the cell is not displaced very far from equilibrium during measurements and (ii) the data from a wide-frequency range can be collected with high precision, offering the possibility to separate different physicochemical processes that are overlapping through different characteristic time constants. During the past three decades, many studies of AC impedance have been conducted to investigate SEI statuses, insertion/de-insertion reactions, and diffusion behaviors. For example, Thomas et al. [10] investigated the insertion electrode $Li_{1-x}CoO_2$; Ho et al. [11] studied lithium diffusion in tungsten trioxide thin films; Levi et al. [12] investigated the kinetics of lithium intercalation into Li_{1-}

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${}_{x}CoO_2$; Takeno et al. [13] gave a quick diagnosis of Li-ion battery packs; Wagg et al. [14] investigated the power capabilities of Li-ion batteries; Zhang et al. [15] studied SEI formations; Osaka et al. [16] evaluated a proposed circuit model in which a growing SEI was taken into account for a commercial LIB through fitting error. All of these studies reviewed above were conducted with an AC impedance approach. As mentioned before, lithium diffusion behaviors, kinetics of charge transfer reactions, and status of SEI layers are all important parameters that determine the rate capabilities and power performances of LIBs [3]. For automobile applications, rate capabilities and power performances are critical for successful technology implementation. Therefore, a quick diagnosis for the above parameters at various values of SOC is necessary for battery management systems in order to guarantee the reliability, safety and efficiency of the battery or ultracapacitor modules [1,4,5]. As far as we know, there are a few investigations of the above parameters for LIBs applied in electric vehicles, in particular for automotive LIBs at various SOC values. Electric vehicle LIBs possesses lower internal resistances, longer diffusion lengths, and larger interfacial areas than that of normal LIBs, leading to more prominent inductance effects, larger diffusion time constants, and further deviations from ideal interfaces than that of normal LIBs.

In this paper, we have conducted a quick but substantial diagnosis of automotive LIBs using fractional impedance spectroscopy with an attempt to gain a fundamental understanding of lithium diffusion behaviors, charge transfer reactions and SEI layer statuses at different SOCs. The constructed fractional impedance model takes all of the intrinsic characteristics of automotive LIB into account. These intrinsic characteristics are mainly comprised of constant phase elements representing non-ideal interfaces [17], semi-infinite Warburg impedances representing lithium solid state diffusions [18,19], and inductance representing high-frequency inductance effects. Fractional impedance modeling plays a critical role in LIBs as well as in ultracapacitors [20], hence we discuss this core question in subsequent two sections of “2.1. Fractional impedance elements” and “3.3. Modeling of fractional impedance spectra”. Through the impedance diagnosis of LIBs presented in this work, we believe that the method developed here should be considered as the general approach for impedance diagnosis of other devices for electrochemical energy storage and conversion in automotive applications.

2. Experimental

2.1. Fractional impedance elements

In our approach, traditional resistance R is expressed as impedance ($Z_R = R$), inductance L as $Z_L = j\omega L$, and capacitance C as $Z_C = \frac{1}{j\omega C}$. The distributed or fractional impedance elements are used to simulate the measured impedance spectra in order to obtain simulation results with higher precision. In order to construct better fractional impedance models so as to gain deeper understanding into the reaction kinetics and diffusion behaviors of automotive LIBs, we analyzed and simulated typical fractional impedance elements such as constant phase elements and diffusion impedance elements with parameters closely related to that of an actual Li-ion battery.

2.1.1. Constant phase elements

Capacitance, an interfacial impedance that can be used to characterize properties of the double-layer region of electrodes/electrolytes, can be induced by a non-faradaic process [21]. Normally, a capacitance (C) in parallel with a resistance (R) produces a semi-circle in a Nyquist plot. However, due to the fraction or roughness of electrode surfaces [17], uneven distribution of reaction rates [22], varying thicknesses or compositions [23], and non-uniform distribution of currents [24], semi-circles are often depressed. Hence, a constant phase element (CPE) is put forth to present the depressed semi-circle. The impedance (Z_{CPE}) of the CPE is given by the following equation:

$$Z_{CPE} = \frac{1}{Q(j\omega)^{\alpha}} \tag{1.1}$$

$$\arg \quad (Z_{CPE}) = -\frac{1}{2}\alpha\pi \tag{1.2}$$

where Q is the amplitude, α is the fractional exponent ranging from -1 to 1, and ω is the angular frequency of CPE. Obviously, the $\arg(Z_{CPE})$ of CPE is independent of ω, which makes it a valuable property to discern CPE. There are four special cases for the exponent factor α:

(i) $\alpha = -1.0$, CPEdegenerates into $Z_{CPE}|_{\alpha=-1} = j\omega Q^{-1}$, equivalent to a pure inductance $L \triangleq Q^{-1}$;
(ii) $\alpha = 0$, CPE degenerates into $Z_{CPE}|_{\alpha=0} = Q^{-1}$, equivalent to a pure resistance $R \triangleq Q^{-1}$;
(iii) $\alpha = 0.5$, CPE degenerates into $Z_{CPE}|_{\alpha=0.5} = \frac{1}{\sqrt{j\omega Q}}$, equivalent to a semi-infinite diffusion Warburg impedance $Z_{W\infty} = \frac{\sigma}{\sqrt{j\omega}}$, where $\sigma \triangleq Q^{-1}$ is the mass-transfer coefficient or Warburg coefficient;
(iv) $\alpha = 1.0$, CPE degenerates into $Z_{CPE}|_{\alpha=1.0} = \frac{1}{j\omega Q}$, equivalent to a pure capacitance $C \triangleq Q$.

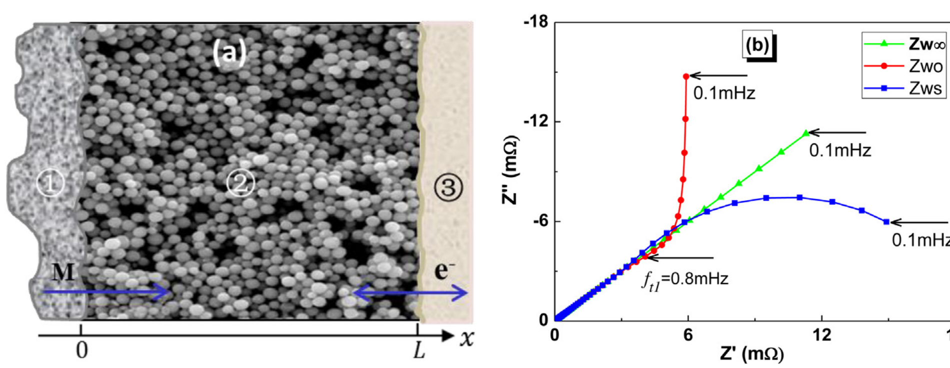

Fig. 1. (a) Scheme of the diffusion of redox species M through the porous electrode; (b) Warburg impedance simulation for $Z_{W\infty}$,Z_{Wo} and Z_{Ws} with frequencies ranging from 0.1mHz to 0.1 MHz. Herein, $\sigma = 3*10^{-4}\Omega s^{-\frac{1}{2}}$, $l = 1*10^{-6}m$, $D = 5*10^{-12}cm^2s$.