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Effect of microstructure morphology on Li-ion battery graphite anode performance: Electrochemical impedance spectroscopy modeling and analysis

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ABSTRACT

Carbon graphite has received much attention over the last decades as the best candidate for negative Li-ion battery electrodes due to its thermal stability and optimal cycling capability. This paper aims to give a comprehensive account of the effect of microstructure morphology such as porosity, tortuosity, solid-electrolyte interface area and active material particle geometry on the overall performance of an electrode. Simulated annealing method (SAM) was used to reconstruct a virtual microstructure of a graphite anode based on different active material particle configuration. The underlying species transport and reaction kinetics of an electrochemical cell were modeled through an electrical circuit composed of different components. Simulated results show that active material particle geometry directly influences the tortuosity and specific surface area of the microstructure, thus affects the solid and electrolyte phase electronic/ionic mobility. Nyquist plot provided an overall impedance of ionic and electronic diffusion over a frequency range of 0.1 mHz to 20 kHz. The semi-circle in the high-frequency region is associated with charge transfer resistance and dielectric behavior of the solid-electrolyte interface (SEI) while the 45° slope at the low-frequency region is a result of lithium diffusion into the solid electrode.

1. Introduction

Li-ion batteries are widely used for consumer electronics due to their high energy to weight ratio, minimal self-discharge, and optimal cycling capability [1,2]. Recent developments in battery chemistry and distributed grid management system extended Li-ion battery application for power storage devices in stand-alone photovoltaic systems and as a power source for electric and hybrid vehicles, thus reducing greenhouse gas emissions from motor vehicles [3,4]. However, there are still some critical issues that have to be addressed to realize mass electrification of road transport vehicles such as cost, safety, limited mileage and extended charging time. Generally, the performance of a Li-ion battery (cell potential and energy density) depend on cell chemistry and electrode microstructure morphology while its safety is mainly determined by the stability of the underlying chemical reactions and uncontrolled dendritic growth at SEI that could damage the separator and leads to the internal short circuit. From microscale point of view, performance optimization of Li-ion battery electrodes includes a systematic design of microstructure morphology parameters such as particle size and shape, porosity, tortuosity and effective solid-electrolyte contact area.

Although many researchers put a huge effort in the search and development of new and existing Li-ion battery anode materials, artificial graphite has been one of the main choices of negative electrodes, due to its high cycling performance, high reversibility and lower cost [5–8]. However, graphite electrodes have some limitations for high-power application due to limited intercalation capacity, a higher rate of lithium plating at the end of charging [9] and evolution of SEI in the graphite surface [10] which is always associated with safety issues. The number of Li-ions inserted into the negative electrode during a single charging that determines the cell/battery potential is greatly influenced by microstructure morphology (particle size, porosity and tortuosity etc.) of the electrode, the electrolyte chemistry and the percentage of Li-ions delithiated from the positive electrode. Comprehensive understanding of the underlying reaction kinetics at SEI and Li-ion diffusion in the electrolyte and solid-state electrode helps in a systematic design

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of electrode microstructure morphology thus, improving its performance and safety [11,12].

The major underlying electrochemical processes take place in an electrochemical system are ionic diffusion in the electrolyte, solid-state electronic diffusion into the solid electrode and the charge transfer in the SEI. Several experimental techniques and electrochemical models have been devised over the last decades to determine the solid-state diffusion coefficient of Li^+. Among the most frequently used techniques are potential intermittent titration technique (PITT), Galvano-static intermittent titration technique (GITT) developed by Weppner et al. [13], transmission line model developed by Levie [14] and electrochemical impedance spectroscopy (EIS) [15,16]. However, the results of different models and experiments do not show consistent results due to the complexity of the underlying electrochemical processes, the lack of reliable theoretical and experimental methods and intricacy of the microscopic surface texture of electrodes. Cho et al. [11] proposed an analytical approach based on the work by Meyers et al. [17] to predict the effect of electrode microstructure on the electrical and ionic conductivity. They found that the microstructural variation directly affects the solid-electrolyte interfacial area, and hence influences the impedance response of the electrodes.

EIS is an experimental study of the response of an electrochemical system to an applied small amplitude perturbation of voltage or current [11,18,19]. The frequency-dependent impedance is used to quantify many underlying physical and chemical processes including ionic transport resistance in the electrolyte, charge transfer in SEI and solid-state diffusion of Li^+ ions into the solid electrode. Since part of these processes are related to the time derivatives of potential difference and current concentration in SEI, some parts of the response are in-phase and some parts are out-of-phase with the applied signal, (current leads or lags the potential) [13]. Hence, the numerical results of the real and imaginary values of the impedance spectra can be represented by Nyquist plot over a wide range of frequency. Equivalent circuit model, composed of resistance, inductance and capacitance (RLC) elements along with a finite-length Warburg (solid-state diffusion) or constant phase element (CPE) has been used in the past [20–22] to describe the impedance response of the electrochemical systems.

The objective of this work is to investigate the effect of electrode microstructures on the effective species and charge transport in the solid and electrolyte phase and to model the overall impedance response of a graphite anode during charge/discharge cycle through an equivalent circuit technique. Simulated annealing method (SAM), a numerical approach was adopted to reconstruct virtual microstructures of Li-ion battery anode electrode based on spherical particles by Wu and Jiang [23] and based on ellipsoid particles by He et al. [24]. In this work, additional two active material particles are introduced namely cylindrical and elliptic cylinder to study a wide variation of microstructure morphologies on the impedance response.

2. Modeling

2.1. Numerical microstructure reconstruction

SAM were used to generate 3D microstructure volume of a graphite anode, based on the principles of metal annealing process, in which the metal is heated to an elevated temperature and allowed to cool slowly to absolute zero until the global minimum energy state (ground zero equilibrium) is achieved. The probability of a system having an energy state E at any given temperature T is given by Boltzmann distribution [25] as follows.

$$P(\delta E) = \exp(-\delta E/T(k)) \quad (1)$$

where k is a small annealing temperature step. Similarly, numerical SAM employs a function that can be used to mimic the energy of practical metal annealing system. Statistical information gained from real microstructures obtained by imaging techniques such as transmission electron microscope (TEM) and scanning electron microscope (SEM) [26] can be used to extract 3D microstructure data. The main input parameters of the reconstruction process are the porosity, active material particle geometry and two-point autocorrelation functions. The two-point autocorrelation function examines the probability of two arbitrary points in a homogenous microstructure laying in the same phase. The image of a typical Li-ion battery graphite anode generated by secondary SEM that contains three-dimensional morphological information is shown in Fig. 1. The active material particles shown in the image resembles flake-like structures having irregular shapes stacking over each other with anisotropic morphological characteristics. Therefore, apart from spherical particles, three other rotational asymmetric active material particles (ellipsoid, cylindrical and elliptic cylinder) were used to mimic the anisotropic characteristics of a real graphite anode.

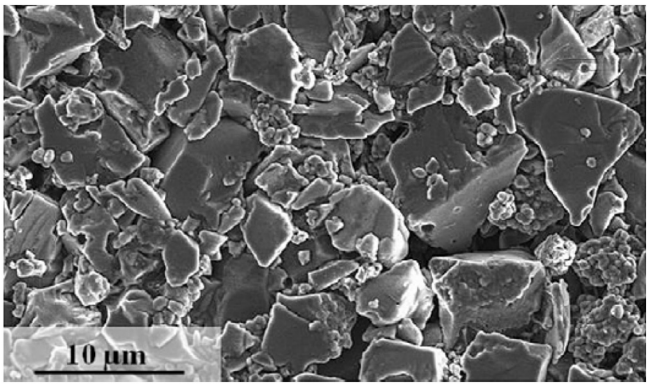

Fig. 1. SEM image of Li-cell anode surface with the binder coating [27].

Unlike spherical particles (which has rotational symmetry), the geometrical orientation of the rotational asymmetric particles in the reconstructed volume is determined by an axis-angle rotation (α, β, and γ) relative to the three orthogonal axes. The morphology of the active material particles and their probabilistic position in the microstructure domain are shown in Fig. 2a and b respectively. The particles rotation angles α, β and γ are constrained between $-\pi/18 \le \alpha \le \pi/18$, $-\pi/18 \le \beta \le \pi/18$ and $0 \le \gamma \le 2\pi$ respectively. This configuration of the particles represents at higher accuracy the stacking arrangement of particles of real graphite anode.

The probabilistic angular position of the asymmetric particles creates a difference at the microstructural morphology between the in-plane (parallel to yz-plane) and the through-plane (perpendicular to yz-plane) directions. Therefore, two two-point autocorrelation functions were applied for the in-plane and through-plane direction, respectively. More information on SAM based on spherical and ellipsoid active material particle can be found elsewhere [23,24].

The reconstructed graphite microstructure domain represents a cube of one million voxels with a single voxel size of 1 μm (i.e. the total volume of the domain is $100 \times 100 \times 100\ \mu m = 1{,}000{,}000\ \mu m^3$) and is composed of an active material, additive (conductive carbon and binder) and pore (i.e. electrolyte). The resolution of the microstructure depends on the relative size of the individual particle and the overall volume of the microstructure. The number of total voxels in the reconstruction domain significantly affects the simulation time and cost. To validate the convergence of the reconstruction process, SAM was compared with stochastic reconstruction method in the model validation section of this paper. The active material morphologies are summarized in Table 1 below.

To illustrate the stochastic behavior of particle size distribution found in real electrode microstructures, the particle sizes used to reconstruct the microstructure volume were normalized based on Gaussian (normal) distribution of standard deviation (σ) of value 2; the mean particle dimensions are listed in Table 1. Furthermore, we used