Sci. Bull. (2016) 61(8):656–664
DOI 10.1007/s11434-016-1048-4

www.scibull.com
www.springer.com/scp

Article

Engineering Sciences

Numerical reconstruction of microstructure of graphite anode of lithium-ion battery

Shaoyang He · Jianbang Zeng · Bereket Tsegai Habte · Fangming Jiang

Received: 15 January 2016 / Revised: 2 March 2016 / Accepted: 3 March 2016 / Published online: 24 March 2016

Abstract Due to the presence of graphite flake cascades, the real graphite anode of Li-ion battery shows non-isotropic characteristic. The present work developed an ellipsoid-based simulated annealing method and numerically reconstructed the three-dimensional microstructure of a graphite anode. The reconstructed anode is a composite of three clearly distinguished phases: pore (or electrolyte), graphite, and solid additives, well representing the non-isotropic heterogeneous characteristic of real graphite anode. Characterization analysis of the reconstructed electrode gives information such as the connectivity of individual phase, the specific interfacial area between solid and pore phase, and the pore size distribution. The effects of the ellipsoid size on the structural characteristics of graphite anode were particularly studied. As the size of the ellipsoidal particle slightly increases, the average pore diameter increases and as a result the specific interfacial area between the solid and pore phase in the reconstructed area decreases; compared with the equatorial radius, the polar radius of ellipsoidal graphite particles has more significant influence on the characteristics of electrode microstructure.

S. He · J. Zeng · B. T. Habte · F. Jiang (✉)
Laboratory of Advanced Energy Systems, CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences (CAS), Guangzhou 510640, China
e-mail: fm_jiang2000@yahoo.com

S. He · B. T. Habte
University of Chinese Academy of Sciences, Beijing 100049, China

Keywords Lithium-ion battery · Graphite anode · Microstructure reconstruction · Simulated annealing method · Ellipsoid particles

1 Introduction

Lithium-ion batteries have been extensively applied in consumer electronics, electric vehicles and grid energy storage systems due to their high energy (power) density and superior performance. However, the performance of lithium-ion batteries still needs to be improved regarding discharge/charge time and safety issues to satisfy the increasing requirements. The batteries used in electric vehicles should charge quickly and provide sufficient energy storage for long driving distance or time [1]. There may be lithium dendrite growth to cause internal short-circuits resulting in accidents due to lithium deposition reaction during overcharging [2, 3] or lithium plating at low temperatures [4–7]. These lead to the development of battery materials and battery electrochemistry [8–12]. Besides, the complex microstructure of electrodes also has a significant effect on the performance of lithium-ion battery [13–15]. Numerical model plays a key role in the research and optimization of the design of lithium-ion batteries. But most of the numerical models focused on the macro processes rather than the fundamental principles of multiple transports during discharge/charge operations [16–19]. The mesoscale numerical models [20–22] of lithium-ion batteries are based on the microstructure of electrodes to simulate and predict the phenomena of multi-physical transport process from a view of mesoscopic pore-scale, in which the material of each voxel is clearly distinguished from each other so as the intrinsic physical property parameters of each individual phase can be specified; the

interface of solid active and electrolyte is clear to describe and dispose the electrochemical reactions and the intercalation/de-intercalation (rocker chair) process of Li atom or ion. Thus it is better to explore and analyze effects of mesoscale microstructure of electrodes (including separator) on the multi-physical transfer process coupled with electrochemical reactions. In particular, with the microstructure reconstruction, the mesoscale model can help to predict the effective transfer properties of electrodes and verify the effect of volume fractions (or size and shape) of material particles on the performance of electrodes. These are also considered as significant references for improving the performance of electrode, of which the intrinsic electronic conductivity is bad, such as the $LiFePO_4$ cathode.

The reconstruction of microstructure is the foundation and precondition of mesoscale model for lithium-ion batteries. The two major ways of microstructure reconstruction involve experimental and numerical approaches. Although the experimental methods can completely truly reflect the real microstructure of electrodes [23–27], they cost enormous time and investment. The numerical models include Gauss stochastic field method [28, 29], simulated annealing method (SAM) [30–35], process-based reconstruction [36] and stochastic grid method [37, 38], etc. Among the above mentioned numerical methods, the SAM can be used to obtain a reconstructed microstructure which is more similar with the real one because it builds an objective function that can be regarded as the "energy" of system, of which the state of minimum energy value can be achieved through the minimization evolution of local energy. In addition, more statistical information of the microstructure could be taken into account by the SAM and it is more convenient to deal with the spatial distribution and bond relationship between solid active materials and additives. Yeong and Torquato [30] came up with the voxels-based SAM in the first place, of which the basic unit of algorithm execution is a collection of discrete voxels in the reconstructed domain. Hejtmánek et al. [31] extracted the two-point correlation function from porous media as statistic information and an important input parameter of reconstruction that describes the characteristic of microstructure. According to the work by Yeong and Torquator [30], Kim and Pitsch [32] developed the SAM based on uniform spherical particles and reconstructed the microstructure of catalyst layer (CL) of proton exchange membrane fuel cell (PEMFC). Further, Wu and Jiang [33–35] developed an SAM in which a size distribution of particles was specified and numerically reconstructed the microstructure of $LiCoO_2$ cathode of lithium-ion battery [33, 34] and a CL of PEMFC [35]. However, the microstructures reconstructed by sphere-based SAM are generally isotropic. The anisotropic microstructure of graphite anode cannot be reconstructed directly by a normal sphere-based SAM.

This paper adapts the SAM developed for the reconstruction of microstructure of $LiCoO_2$ cathode by Wu and Jiang [33, 34], and takes the shape of flaky graphite particles into account and develops an ellipsoid-based SAM to numerically reconstruct the anisotropic microstructure of graphite anode. The characteristics of reconstructed microstructure are analyzed to discuss the effects of size and shape of the ellipsoid particles on the structural characteristics of graphite anode.

2 The feature and numerical description of graphite anode

During the reconstruction of $LiCoO_2$ cathode in lithium-ion battery with the SAM [33, 34], there are two assumptions taken into account: (1) the microstructure of electrode is isotropic; (2) the solid active material particle is spherical. These two assumptions are much more likely not appropriate for the graphite anode. The microstructure of the graphite anode [39], as depicted in Fig. 1a, in which the graphite particles are flat and conglutinated together with conductive agent and binder materials, is evidently non-isotropic, sharply differing from the morphology of microstructure of cathode (Fig. 1b).

In the reconstructed microstructure, the conductive agent and binder materials are regarded as the solid additives and the electrode can thus be simplified as a three-phase composite consisting of pore, graphite and additives. The reconstructed volume of the electrode is divided into a sequence of grid voxels described with phase function:

$$I_i(r) = \begin{cases} 1, & \in \text{ phase } i, \\ 0, & \text{otherwise}, \end{cases} \tag{1}$$

where $\boldsymbol{r}(x, y, z)$ is an arbitrary position vector in a 3D space (reconstructed area of graphite anode); $i = 0, 1, 2$ with 0 denoting pore phase, 1 graphite and 2 solid additives.

The relevant structural information of each phase can be obtained by computing the statistical mean value: porosity $\varepsilon_0 = <I_0(r)>$, volume fraction of each component $\varepsilon_i = <I_i(r)>$ and two-point correlation function $f_{ij}(r_1, r_2) = <I_i(r_i)I_j(r_j)>$ [40]. Among the above, the two-point correlation function is the possibility of that the phase at position r_1 is i while the phase at position r_2 is j in the reconstructed domain. It reflects the relationship between the spatial distributions of phases. With the assumption of isotropic electrode, the two-point correlation function can be simplified as the function of the distance between the two positions. In this paper, the direction along thickness of electrode is set to be parallel to x axis and the other two directions perpendicular to x axis parallel to y and z axis respectively. The morphology of microstructure of graphite anode is obviously anisotropic as a whole whereas