Journal of Power Sources 282 (2015) 572–580

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

An extended homogenized porous electrode model for lithium-ion cell electrodes

Moses Ender

Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe Institute of Technology (KIT), Adenauerring 20b, 76131 Karlsruhe, Germany

HIGHLIGHTS

- 1D extended porous electrode model for modeling realistic electrode structures.
- Uses a maximum of microstructure information from 3D reconstructions.
- The model includes the coupling between particles of different sizes.
- The model includes the effect of a resistive surface layer (SEI).
- Provides an explanation for vanishing graphite potential plateaus at high currents.

ARTICLE INFO

Article history:
Received 27 October 2014
Received in revised form
25 January 2015
Accepted 17 February 2015
Available online 18 February 2015

Keywords:
Lithium-ion
Porous electrode model
Particle size distribution
Simulation
Microstructure reconstruction

ABSTRACT

A new 1D lithium-ion cell electrode model is presented, which, for the first time, considers the electrochemical coupling between particles of a real particle size distribution obtained from tomography data. It does so without actually resolving the 3D electrode microstructure in the model, but by including all necessary information in a homogenized manner, using microstructure data from high-resolution X-ray tomography. Additionally, the transport of lithium through the solid-electrolyte interphase (SEI) is considered. The effects of the particle–particle coupling are shown for a graphite negative electrode from a cylindrical high-power cell. The extended homogenized 1D porous electrode model provides an explanation for the vanishing plateaus in the graphite potential curve with increasing charge or discharge rates. This effect is not covered by state-of-the-art models.

1. Introduction

Since their commercialization in the 1990s, lithium-ion batteries have become the most important electrochemical energy storage system. They can now be found in practically every mobile device, as well as in most electric or hybrid electric vehicles.

There are still many unanswered questions, despite their wide distribution in commercial applications, e.g.:

(a) which mechanisms take place on the different length-scales of a lithium-ion cell, and
(b) what role does the electrode microstructure play in the coupling of the different physical, chemical and electrical processes?

The rapidly growing field of microstructural studies using different tomographic techniques delivers highly detailed three-dimensional information about these electrode microstructures. Thanks to steadily increasing computing powers, it is in principle possible to use these reconstruction data directly as model geometries [1,2]. Fig. 1 shows simulated lithium distributions in a graphite electrode of a commercial cell at two different times during charging with C/10. A detailed insight into the local lithium concentration c_{Li} after t = 5.1 h is given in Fig. 1d, e and after t = 8.9 h in Fig. 1f, g, which corresponds the end of charging at a anode potential of 0.05 V vs. Li. Obviously, the graphite electrode of a commercial cell consists of individual particles widely distributed in size. As the lithium intercalation starts at each particle's surface at the same time and with the same diffusion constant, after charging with C/10 the larger particles are not completely filled with lithium, whilst the small particles are. Naturally, such an inhomogeneous lithium concentration influences the dynamic

---

E-mail address: moses.ender@kit.edu.

http://dx.doi.org/10.1016/j.jpowsour.2015.02.098
0378-7753/

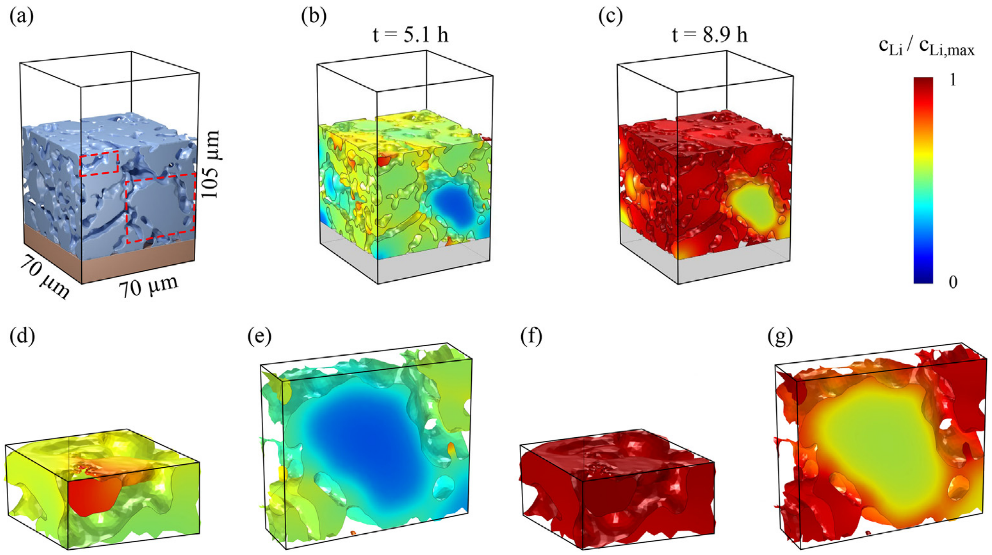

Fig. 1. Spatially resolved simulation of the graphite anode charging process. (a) The microstructure used as model geometry was analyzed by X-ray tomography and reconstructed with the help of appropriate algorithms [3]. The simulated lithium concentration c_{Li} for charging with C/10 is shown. (b)At the middle of charging (t = 5.1 h), small particles (d) have almost reached the maximum lithium concentration, while larger particles (e) are still almost empty. (c) When the end-of-charging potential (0.05 V vs. Li) is reached (t = 8.9 h), small particles (f) are completely filled with lithium, but larger particles (g) are not. The simulation was performed with COMSOL Multiphysics on a high-performance workstation.

electrode behavior in a commercial cell and should be taken into consideration.

The simulation was performed with COMSOL Multiphysics and took about three days on a high-performance workstation with 32 CPU cores and 256 GB memory. The 3D microstructure used as model geometry was obtained by X-ray tomography and reconstructed with the help of appropriate algorithms [3]. It has to be mentioned at this point that the particles of this 3D microstructure have not been individualized. In fact the structure used for this simulation consists of a connected geometry with no extra resistances assumed between the particles.

Even though, calculation time on a supercomputer would be much less, for the time being such highly detailed 3D models are not ideal for extended parameter studies or model-driven electrode engineering.

For that reason, most published parameter studies were performed using homogenized 1D porous electrode models [4,5]. These assume only one average particle size to be representative for the whole electrode structure, disregarding the contribution of the small and the large particles. The simulation result shown in Fig. 1 underlines, that such a simplified approach cannot properly describe the charging and discharging of an electrode in a commercial cell, as it neglects the interaction of particles with different sizes.

For that reason, the proposed modeling approach includes the essential information of particle size distribution and extends a well-established 1D homogenized model, which contains all important reaction and transport mechanisms in the electrode. Fig. 2 illustrates the experimental procedure, which delivers the microstructure parameters. An electrode from a commercial cell is extracted and reconstructed by a tomographic method. The 3D reconstruction dataset is then analyzed by appropriate algorithms and obtained particle size distribution is used to parameterize the extended 1D porous electrode model [3]. In this 1D model, the particle size distribution information is included in each electrode volume element. Therefore, interaction is possible between particles of different sizes, in contrast to state-of-the-art 1D porous electrode models.

The approach of dividing the overall charge transfer current into several contributions from different particles has been tested by Newman et al. for two discrete particle sizes [6] and for a blend electrode consisting of two particles with different electrochemical properties [7]. This work presents for the first time an extended 1D porous electrode model capable of reflecting real particle size distributions obtained from tomography data without spatially resolving the complete electrode microstructure. It does so by exploiting information obtained from high-resolution microstructure reconstructions and using it within a volume-averaged 1D porous electrode model.

2. Modeling

2.1. Electrochemical model

The electrochemical model used to describe the graphite electrode is based on equations proposed by Newman et al. [8]. Here, we focus on the anode half-cell, which means that the model describes just one electrode with respect to an imaginary lithium reference electrode, placed in the middle of the separator. In the following, a short description of the included transport and reaction processes is given.

The liquid electrolyte consists of a lithium salt (with $z_+ = -z_- = 1$) dissolved in an aprotic solvent. Transport within this is modeled by the theory of concentrated binary electrolyte, as developed by Newman [9]. This includes diffusive transport as well as migration in the electric field:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D_{amb} \nabla c_l) - \frac{\vec{j}_l}{F} \nabla \cdot t_+ \tag{1}$$

where c_l is the salt concentration in the liquid phase, D_{amb} is the ambipolar diffusivity and t_+ the cation transference number; which are calculated as:

$$D_{amb} = \frac{2D_+ D_-}{D_+ + D_-} \tag{2}$$