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A theoretical model to determine the capacity performance of shape-specific electrodes

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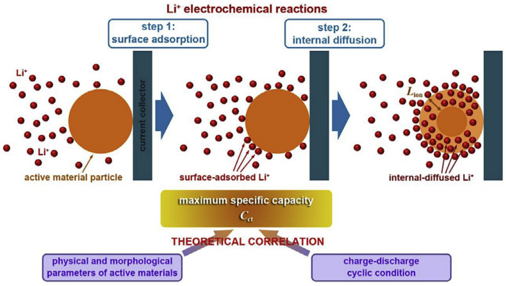
HIGHLIGHTS

- A model to explain the electrochemical process of lithium-ion batteries is built.
- A formula to denote the maximum capacity at different C-rates is derived.
- Reducing particle size and C-rate can provide greater capacity output.
- The theoretical model is validated by related published experimental results.

GRAPHICAL ABSTRACT



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ABSTRACT

A theory is proposed to explain and predict the electrochemical process during reaction between lithium ions and electrode materials. In the model, the process of reaction is proceeded into two steps, surface adsorption and diffusion of lithium ions. The surface adsorption is an instantaneous process for lithium ions to adsorb onto the surface sites of active materials. The diffusion of lithium ions into particles is determined by the charge-discharge condition. A formula to determine the maximum specific capacity of active materials at different charging rates (C-rates) is derived. The maximum specific capacity is correlated to characteristic parameters of materials and cycling – such as size, aspect ratio, surface area, and C-rate. Analysis indicates that larger particle size or greater aspect ratio of active materials and faster C-rates can reduce maximum specific capacity. This suggests that reducing particle size of active materials and slowing the charge-discharge speed can provide enhanced electrochemical performance of a battery cell. Furthermore, the model is validated by published experimental results. This model brings new understanding in quantification of electrochemical kinetics and capacity performance. It enables development of design strategies for novel electrodes and future generation of energy storage devices.

1. Introduction

In comparison of existing methods, the electrochemical energy storage is the most practical and reliable approach to store the energy as electricity [1–3]. Its advantages of convenient portability, extended durability, and high energy density are driving forces. Lithium-ion batteries (LIBs) have made it possible to serve as the most popular rechargeable electrochemical energy storage devices since early 1990s [4]. The high energy and capacity densities, stable power output, and controllable size of LIBs ensures their widespread applications to portable personal electronics, electric and hybrid vehicles, and among others [1].

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The electrochemical performance of the electrode materials (including cathode and anode) is critical in design LIBs. Performance parameters such as higher electric conductivity, greater surface area, smaller particle size, improved reaction kinetics, and more stability under fast cyclic speed, are the goals to improve electrodes [5]. The potential ability of the capacity output of a specific LIB cell under a specific cycling condition is an important criterion to justify its electrochemical performance. Researchers usually use the term of "theoretical specific capacity" as a reference value to identify the performance [6]. In recent decades, an increasing number of novel electrode materials with nanostructures, shape-specific morphologies, and hierarchical architectures have been manufactured with versatile performance [7–9]. However, for all types of electrode materials, conventional understanding about specific capacity can only provide a general reference basis of their performance [6]. No detailed statuses such as structure, size, surface area, and cyclic C-rate are included. Therefore, for electrode materials, a quantitative theoretical model to correlate the maximum specific capacity to the parameters of the electrode and charge-discharge condition is necessary to be proposed. A model is expected to answer the following questions: 1) what is the maximum capacity of the electrode with a certain morphology used at a C-rate? 2) how to select the dimension, size, and aspect ratio for an electrode material to reach an expected goal of the capacity performance? and 3) what is the fastest acceptable C-rate to produce a proposed capacity value for an electrode?

In this research, we derived a theoretical model to determine the maximum specific capacity of one shape-specific electrode material under a different cyclic conditions. Two steps of the electrochemical reaction between lithium ions and active materials were considered to construct the model. The first step is surface adsorption of lithium ions, and the second is their internal diffusion into the active material. As a result, an equation to quantify the value of the maximum specific capacity was derived as the function of characteristic parameters of active material particles (including particle size, aspect ratio, and specific surface area) and the C-rate value. Through systematic analysis, it was identified that to achieve maximum capacity, the smaller the particle size, or the lower the aspect ratio, the slower the C-rates. Moreover, the model was validated by experimental data of 25 published reports on various morphology and materials. The theoretical model is applicable to general LIB electrode materials with morphological and compositional diversity. In summary, this theoretical model provides a practical approach to design a LIB cell with the maximum capacity and best charge-discharge performance.

2. Model construction

The theoretical model is based on a scenario of an electrode made of particles of the active material (marked as AM). This AM has a molar mass of M (in kg mol^{-1}) and bulk density of ρ (in kg m^{-3}). After applying an external potential with the current density at a C-rate of ζC, the AM electrode will react with lithium ions inside a liquid (non-aqueous or aqueous) electrolyte of a LIB cell. If AM is a cathode, then the reaction is insertion of lithium ions (Equation (1)); if AM is an anode, then the reaction can be insertion (Equation (2)), alloying (Equation (3)), or conversion (Equation (4)) depending on the type of material. Please note that the parameter x, i.e. the transferred number of electron per reaction, is not necessarily to be an integer. The theoretical maximum specific capacity of AM at C-rate of ζC is denoted as C_{ct} (in mAh g^{-1}). The theoretical analysis of the electrochemical reaction between AM and lithium ions is divided into two steps. The first step is the reaction during the surface adsorption of lithium ions; the second step is the reaction during the internal diffusion of lithium ions. Fig. 1 illustrates the process with above two steps.

$$\text{Cathode:}x\text{Li}^+ + xe^- + \text{M}_n\text{X}_m \leftrightarrow \text{Li}_x\text{M}_n\text{X}_m,\quad \text{M= metals},\quad \text{X= O, S, etc.} \tag{1}$$

$$\text{Anode with insertion:}x\text{Li}^+ + xe^- + x\,\text{C} \leftrightarrow \text{Li}_x\text{C}_x \tag{2}$$

$$\text{Anode with alloying:}x\text{Li}^+ + xe^- + \text{M} \leftrightarrow \text{Li}_x\text{M},\quad \text{M= Si, Ge, or Sn.} \tag{3}$$

$$\text{Anode with conversion:}2m\text{Li}^+ + 2me^- + \text{M}_n\text{X}_m \leftrightarrow n\,\text{M}+ m\text{Li}_2\text{X},\quad \text{M= metals},\quad \text{X= O, S.} \tag{4}$$

The contact between lithium ions in the electrolyte and solid AM surface is the precondition of the above reactions in Equations (1)–(4). This contact can be considered as type of liquid–solid Langmuir adsorption [10]. The electrochemical reaction is triggered immediately after the adsorption occurs (as shown in Fig. 1b). The total specific surface area is denoted as A_s (in m^2 mol^{-1}) for 1 mol of AM electrode (with N_A molecules or crystalline unit cells). For the Langmuir adsorption of lithium ions, there are n available surface sites per unit area of AM. For most of solid materials, the value of n is usually at the order of magnitude of 10^{18} sites per m^2 [11]. Then the total number of available surface sites in 1 mol of AM electrode is $A_s \cdot n$.

According to the theory of Langmuir adsorption, the fractional occupancy of the adsorbed lithium ions at the equilibrium θ_s is denoted as Equation (5):

$$\theta_s = \frac{K_{eq}c_{Li}}{1 + K_{eq}c_{Li}} \tag{5}$$

where c_{Li} is the concentration of lithium ions in the electrolyte, K_{eq} is the equilibrium constant of reactions of Equations (1)–(4). It is straightforward that K_{eq} can be simply written as Equation (6) for any type of reaction in Equations (1)–(4). In this case, the expression of θ_s can be rewritten as Equation (7). Therefore, the total number of surface sites that participate in the electrochemical reaction between lithium ions and AM N can be derived as Equation (8). Due to xe^- is transferred for each reaction site, the total number of e$^-$ transferred in the step of surface adsorption of lithium ions per mole AM electrode is expressed as $N_e{}^s$ in Equation (9).

$$K_{eq} = \frac{1}{[\text{Li}^+]^x} = \frac{1}{c_{Li}^x} \tag{6}$$

$$\theta_s = \frac{K_{eq}c_{Li}}{1 + K_{eq}c_{Li}} = \frac{c_{Li}^{1-x}}{1 + c_{Li}^{1-x}} < 1 \tag{7}$$

$$N = A_s \cdot n \cdot \theta_s \tag{8}$$

$$N_e^S = N \cdot x = A_s n x \theta_s \tag{9}$$

The value of actual specific surface area A_s is correlated to the morphological feature of the particles of AM electrodes. Here in this study, the value of A_s is determined based on 1D, 2D, and 3D morphologies of AM micro- or nano-particles. Fig. 2 demonstrates three typical shapes of 1D rods, 2D sheets, and 3D spheres owned by AM particles. For each type of shape in Fig. 2, the smallest dimension of one single particle is defined as r (in meters). The ratio between larger dimension(s) and the smallest dimension is denoted as the aspect ratio of μ. Obviously, μ should be equal or greater than 1 in this case. Fig. 2 marks the length, width, and thickness of the 1D rod, 2D sheet, and 3D sphere. For the ideal case of perfect monodispersion of AM particles, i.e. all AM particles have the identical values of r and μ, the value of A_s per mole AM can be calculated as Equation (10) (detailed derivation of Equation (10) is provided in Supplementary Information). Therefore, the expression of $N_e{}^s$ can be rewritten as Equation (11) for the perfectly monodispersed AM particles.

$$A_s = \frac{2 + \mu}{\mu} \cdot \frac{2M}{\rho r} \tag{10}$$

$$N_e^S = \frac{2 + \mu}{\mu} \frac{2M}{\rho r} n x \theta_s \tag{11}$$

The second step of internal diffusion of lithium ions is the main contributor of the transferred electrons after the process of surface