

Mathematical modeling of hysteresis in porous electrodes

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Abstract We study the mathematical model of the Li⁺ ions' intercalation from the electrolyte into the porous graphite surface of the negatively charged electrode and further Li diffusion inside the electrode particle. For proper approximation of experimental data we use the cubic polynomial. We prove the multiplicity of the steady state solutions in a certain range of the electrode potential values. This multiplicity may be explained by the simultaneous existence of several phases at the graphite electrode surface. Numerical investigation allows us to demonstrate the experimentally observed hysteresis. After including the diffusion of Li into the model we compare the charging time for various electrode structures.

Keywords Butler–Volmer equation · Steady state solution · Multiplicity · Diffusion · Symmetry

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1 Introduction

Investigation of the electrode processes is very important for research and development of lithium-ion batteries. Such batteries demonstrate the highest energy density

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and voltage level among the rechargeable sources, but at the same time they quickly lose their capacity, mainly due to the metallic lithium deposition on the electrode surface.

Porous carbon electrodes are loose conglomerations of roundish particles that accumulate the Li^+ ions from the surrounding electrolyte or return them back. Mathematical models for these processes (intercalation and deintercalation) have been recently proposed by several research groups, for example [1, 3, 8]. But all these models do not explain such experimentally observed phenomena as hysteresis and current density pulses [2].

For this reason we introduce a new mathematical model of Li intercalation and deintercalation in the carbon negative electrode. At the first step we consider the Butler–Volmer equation, which couples the electrode potential, the concentration of Li ions at the electrode surface and the flow of lithium. For our model we take experimental data from [5] and approximate the overpotential dependence on the lithium concentration with a cubic polynomial using the least square method. Unlike [4–6], our model yields the multiplicity of steady state solutions and the possibility of switching from one such state into another with a jump.

Then we add to our model the diffusive effects. It is well known that the density of lithium inside the electrode strongly depends on its structure. It is established experimentally that the micron-size carbon electrode particles may form flat layers, threads or shapeless clods; see [4–6]. Respectively we consider three variants of one-dimensional diffusion in the direction perpendicular to the electrode surface: Cartesian (into the flat layer), cylindrical (into the thread) and spherical (into the particle inside the clod). We write down the diffusion equation with respect to the lithium concentration only; the electric potential is supposed to be constant due to the good conductivity of graphite. At the inner (left) border we set the zero-flux boundary condition, while at the outer (right) border we apply the same Butler–Volmer equation, which now plays the role of the boundary condition. Such model allows us to study the influence of electrode structure on the time of charging.

2 Mathematical models

For proper understanding the dynamics of the diffusive process first of all we should find its steady states. Initially we restrict ourselves to considering the intercalation of the Li^+ ions on the graphite surface of the negative electrode and ignore the diffusion into it:

$$\frac{d\theta}{dt} = \frac{i_{ref}^0}{F \cdot C_{max}} \cdot \left[(1 - \theta) - \theta \cdot \exp\left(\frac{F}{RT}(V - U^0 + S(\theta))\right) \right] \cdot \exp\left(-\frac{1}{2} \frac{F}{RT}(V - U^0 + S(\theta))\right). \quad (1)$$

This process is described by the Butler–Volmer equation (1) from [5]. Here $\theta = \theta(t)$ is the normalized concentration of the Li^+ ions at the electrode surface, $0 \leq \theta \leq 1$; $C_{max} = 1.8 \times 10^{-2} \text{ mol cm}^{-3}$ is the theoretically maximal value of unnormalized

concentration; $U^0 = 8.17 \times 10^{-1} \text{ V}$ is the equilibrium electrode potential; the parameter V is the carbon electrode potential with respect to the reference electrode; $i_{ref}^0 = 1.0 \times 10^{-3} \text{ A cm}^{-2}$ is the reference exchange current density; $F = 9.6485 \times 10^4 \text{ C mol}^{-1}$ is the Faraday's constant.

The function $S(\theta)$ describes the dependence of the electrode overpotential on its surface occupancy with lithium. This dependence has been determined experimentally several times by various research groups; for example [4–6]. We also use their data, but we replace the 6th order polynomial, suggested by the authors, with the cubic one: $S(\theta) = a_1 \cdot \theta + a_2 \cdot \theta^2 + a_3 \cdot \theta^3$, where $a_1 = 3.85784$, $a_2 = -6.39138$, $a_3 = 3.24005$. It approximates experimental results with the absolute error $< 4.0 \times 10^{-3}$.

An important feature of our approximation is the existence of the S-shaped region, as it is shown in Fig. 1. There are multiple values of θ , and thus three steady state solutions to (1) for the potential V belonging to $[V_{min}, V_{max}]$. Most probably this multiplicity appears due to the simultaneous existence of several phases in the structure of the electrode surface as it is reported in [3, 7].

We extend model (1) by taking into account the diffusion of the intercalated lithium into the electrode particle. Let the single spatial variable r , $0 \leq r \leq R_{max}$, be directed perpendicularly to the particle surface. After adding diffusion along r we get the following problem:

$$\frac{\partial \theta}{\partial t} = \frac{D}{r^n} \frac{\partial}{\partial r} \left[r^n \frac{\partial \theta}{\partial r} \right]; \quad t > 0; \quad 0 < r < R_{max}; \quad n = 0, 1, 2; \quad (2)$$

$$\partial \theta / \partial r(t, 0) = 0; \quad (3)$$

$$D \frac{\partial \theta}{\partial r}(t, R_{max}) = \frac{i_{ref}^0}{F \cdot C_{max}} \cdot \left[(1 - \theta) - \theta \cdot \exp \left(\frac{F}{RT} (V - U^0 + S(\theta)) \right) \right] \cdot \exp \left(-\frac{1}{2} \frac{F}{RT} (V - U^0 + S(\theta)) \right); \quad (4)$$

$$\theta(0, r) = \theta_0(r). \quad (5)$$

Lithium slowly diffuses and redistributes along r , moving from the outer border inside the particle in case of intercalation and vice versa in case of deintercalation. The direction of the flow at $r = R_{max}$ is given by (4), which is basically the same Butler–Volmer equation as in (1), but now works as the boundary condition.

From Fig. 1 and Eq. (4) it is easily seen that:

- 1) for $V < V_{min}$ the sign of $\partial \theta / \partial r(t, R_{max})$ is positive when $0 < \theta(t, R_{max}) < \theta_{upper}(V)$ and the dominant behavior of the model is intercalation; the value of θ at $r = R_{max}$ grows till it reaches θ_{upper} ; then $\theta(t, r)$ distributes evenly along r till it reaches the equilibrium solution $\theta(t, r) \equiv \theta_{upper}$;
- 2) for $V > V_{max}$ the sign of $\partial \theta / \partial r(t, R_{max})$ is negative when $\theta_{lower}(V) < \theta(t, R_{max}) < 1$ and the dominant behavior of the model is deintercalation; the value of θ at

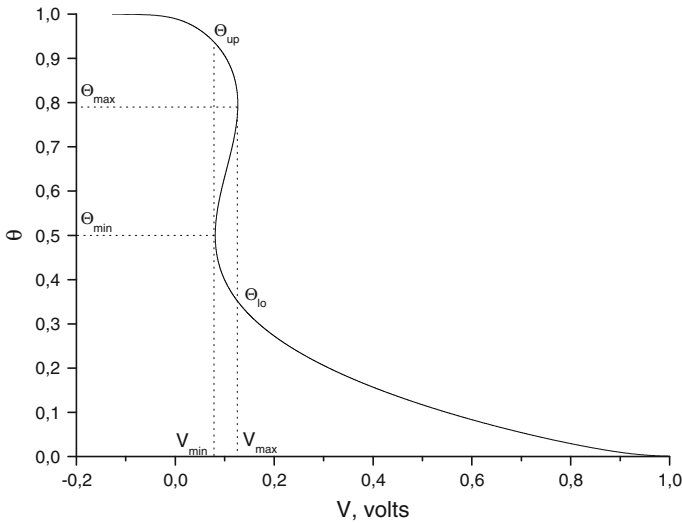


Fig. 1 Steady state solutions to (1) as a graph of θ versus V

$r = R_{max}$ falls till it reaches θ_{lower} ; then $\theta(t, r)$ distributes evenly along r till it reaches the equilibrium solution $\theta(t, r) \equiv \theta_{lower}$;

- for $V_{min} < V < V_{max}$ the sign of $\partial\theta/\partial r(t, R_{max})$ changes thrice when θ runs from 0 to 1; there is no dominant behavior and $\theta(t, r)$ may tend either to θ_{upper} or to θ_{lower} depending on the initial distribution $\theta_0(r)$.

The values of diffusion coefficient $D = 1.0 \times 10^{-9} \text{ cm s}^{-2}$ and the particle size $R_{max} = 10^{-3} \text{ cm}$ are taken from [5]. Being not a surface, but a volume phenomenon, diffusion determines the characteristic time of intercalation, while the upper and the lower stable steady state values of θ follow from the surface boundary condition (4).

3 Numerical results

The curve $\theta = \theta(V)$ in Fig. 1 is obtained by equating to zero the right hand side of (1). It is easily seen that there are three steady state solutions for $V_{min} < V < V_{max}$. The upper and the lower states are stable, while the middle one is unstable. Samples of switching from one steady state to another are shown in Fig. 2:

- Trajectory A starts from $(V_{max} + \delta, \theta_{max})$, $0 < \delta \ll 1$; it's a jump ($\tau_{\downarrow} \approx 1.7 \times 10^{-2} \text{ s}$) from $\theta = \theta_{max}$ to $\theta = \theta_{lower}$.
- Trajectory B starts from $(V_{min} - \delta, \theta_{min})$, $0 < \delta \ll 1$; it is also a sufficiently quick jump ($\tau_{\uparrow} \approx 2.9 \times 10^{-2} \text{ s}$) from $\theta = \theta_{min}$ towards $\theta = \theta_{upper}$.

As a result, a small perturbation of the electrode potential ($V_{max} - V_{min} + 2\delta \approx 0.05 \text{ V}$) causes a sharp variation of the surface concentration of lithium ($\Delta\theta \approx 0.5$). Similar jumps were observed experimentally, for example, in [2], but haven't been yet reproduced in mathematical modeling. The simultaneous existence of three steady state solutions to (1) when $V_{min} < V < V_{max}$ also yields the concentration hysteresis:

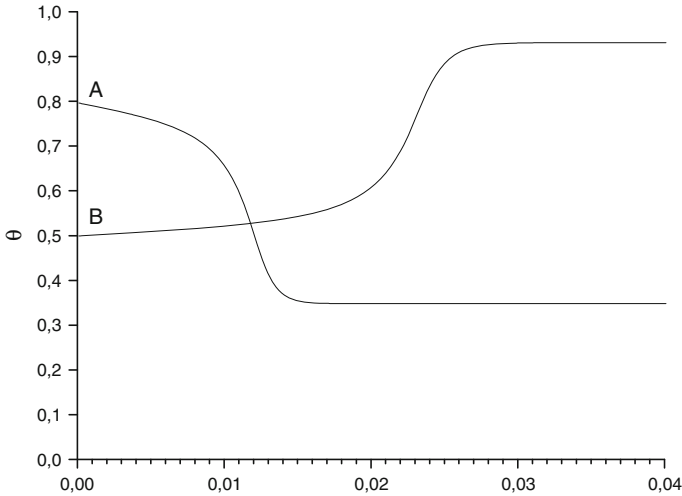


Fig. 2 Switching between the upper and the lower stable steady states in (1)

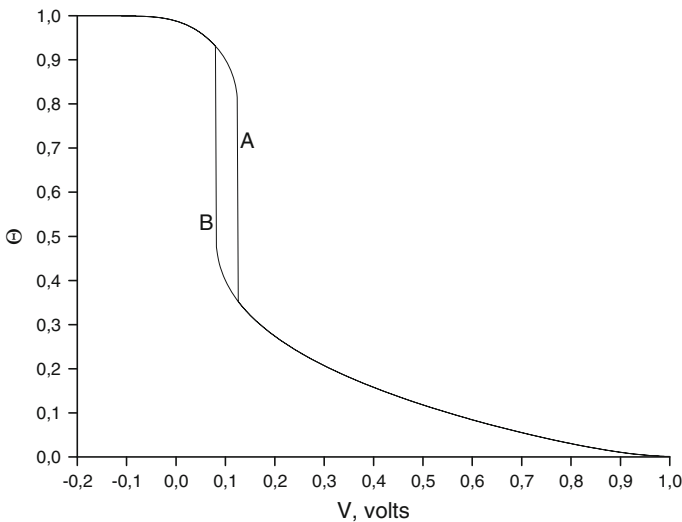


Fig. 3 Hysteresis: a non-unique dependence of concentration versus the potential

the values of the time-dependent solution $\theta = \theta(t)$ may be different for the same value of V . Let us suppose that V slowly varies with time according to the following law: initially $V(t) = V_0 + \nu \cdot t$, while $V(t)$ changes from V_0 to V_1 ; then $V(t) = V_0 - \nu \cdot t$, while $V(t)$ changes back from V_1 to V_0 ; let $\nu = 2 \times 10^{-5} \text{B s}^{-1}$, $V_0 = -0.2\text{V}$, $V_1 = 1.0 \text{V}$.

Solving (1) numerically with such $V(t)$, we see that the trajectory is quickly attracted to the stable steady state θ , which corresponds to the current value of V . But when the potential increases, the concentration follows the upper branch (curve A in Fig. 3), and when the potential decreases, the concentration follows the lower branch (curve B in Fig. 3). Such hysteresis was observed in experiments and described in [2].

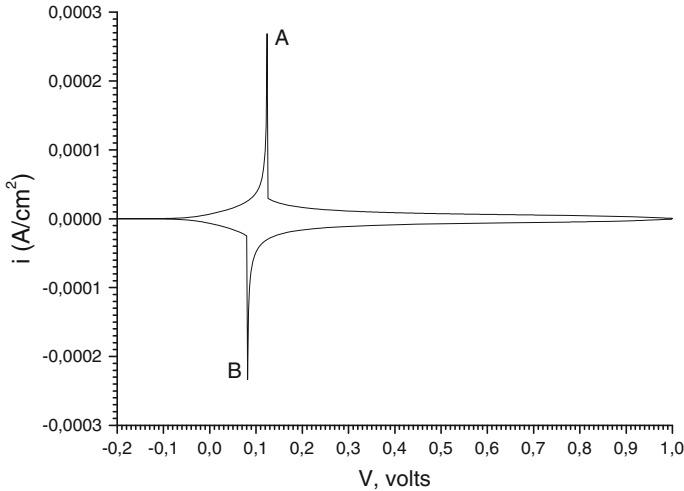


Fig. 4 The pulses: current density with respect to the potential

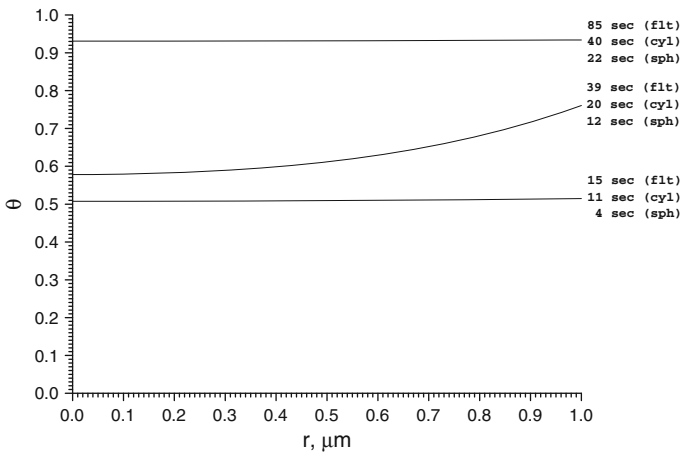


Fig. 5 Diffusion in case of flat, cylindrical or spherical symmetry

In model (1) we've got also the qualitative agreement with experimental data for the dependence of the current density $i(t)$, which equals $F \cdot C_{max} \cdot d\theta/dt$, on the potential $V(t)$, as it is shown in Fig. 4. This model gives correct switching values of the potential: the current pulses in [2] appear at $V_{\downarrow} \approx 0.10$ and $V_{\uparrow} \approx 0.07$ V, while model (1) yields $V_A \approx 0.12$ and $V_B \approx 0.08$ V (see Fig. 4). At the same time the computed values of the current density are nearly twice less than experimental ones.

Numerical results for the diffusive model (2)–(5) were obtained for the initial distribution $\theta(0, r) = \theta_{min}$ and the initial potential value $V = V_{min}$; then the potential started changing according to the law $V(t) = V_{min} - v \cdot t$. The qualitative picture in the cases of flat, cylindrical and spherical symmetry ($n = 0, 1$ and 2 respectively) remained

the same: concentration jumped from the lower to the upper steady state in form of a wave moving from the outer border to the inner one, as shown below in Fig. 5.

In Fig. 5 we see three distributions of lithium: at the initial, intermediate and final stages of switching. The shapes of the curves θ versus r in cases of the flat, cylindrical and spherical symmetry are practically identical, but the moments of time, when they are obtained, are very different: 15, 39 and 85 s for flat case; 11, 20 and 40 s for cylinder case; 4, 12 and 22 s for spherical case respectively. It means that the switching time strongly depends on the form of the particle, because all other parameters remain the same.

The system (2)–(5) was approximated using the symmetric finite difference scheme with the second order of accuracy with respect to t and r . The obtained algebraic equations were solved with Seidel iterations on every time step keeping the absolute error $<10^{-10}$. Comparing numerical results for (2)–(5) with those obtained for (1), we may conclude that taking into account the diffusion radically increases the switching time of the model, from $\sim 10^{-2}$ to $\sim 10^1$ s, but doesn't change the steady state values of θ . Also it is easily seen that the type of symmetry is important: the switching times in the flat, cylindrical and spherical symmetry cases differ by several times for the same particle size and diffusion coefficient

4 Conclusion

We've carried out mathematical modeling of lithium intercalation into carbon electrode particles basing on the experimental data from [4–6]. We state that in a certain range of the electrode potential this process possesses three steady states simultaneously. It may cause hysteresis and quick jumps from one such state into another under small perturbations of the potential. The steady state values are determined by the overpotential dependence on the lithium concentration at the electrode surface, while the characteristic time of switching from one such state into another is determined by the rate of the volume diffusion of lithium, by the size of the electrode particles and by their spatial ordering.

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