Simulation of Lithium Battery Discharge

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Abstract—The discharge of a battery based on a porous Li$_2$TiS$_3$ is simulated. The effect of the electrode geometry on the maximum discharge current is studied. A substantial increase in the specific characteristics is predicted for cylindrical and spherical electrodes, which is attributed mainly to the difficulty of formation of a depleted region remote from the electrode surface. The deviation between experimental current values and the theoretical prognosis is counteracted by using an effective diffusion coefficient that takes into account complex, irregular structures of pores along which lithium transport mainly proceeds.

FORMULATION OF THE PROBLEM

In this work, we study the discharge processes of a battery when lithium ions diffuse from a liquid electrolyte to a porous electrode based on titanium dichalcogenide.

Simulation of processes in the porous electrode—electrolyte system suggests the consideration of a complex of interrelated processes that occur on the background of the complex geometry of the system, which makes it difficult to formulate rigorously the corresponding mathematical problems. The inevitable simplifications, which nonetheless retain the main physical characteristics of the initial object, usually consist in considering a set of models each permitting a sufficiently rigorous formulation. The real system corresponds to one of the intermediate situations whose features might be predicted by the corresponding interpolation formulas.

The system considered consists of an ingot of a porous electrode material with a high conductivity. The geometry of the ingot is characterized by a single macroscopic parameter $L$ (the characteristic size). In different situations, the ingot can have the shape either of a plate bounded by planes spaced $2L$ apart, a cylinder, or a sphere of $L$ radius. For each of these cases, we can formulate models describing different microstructures of electrodes consisting of equidistant microparticles with a characteristic size $r$, plates of $2r$ thickness and cylinders or spheres of radii $r$. It should be noted that the cylindrical model might also be adequate when the geometric dimensions of microparticles are small, but due to the anisotropy of properties, the transport through the edges can be neglected, just as in the case of electrodes of laminated materials with a pronounced anisotropic character of diffusion.

The systems with macroscopic electrode geometry listed above were discussed in [1] in the context of simulating compact electrodes. In this case, the effect of geometric factors of the system on the physical parameters of the battery proved significant.

In this work, we carried out the mathematical simulation of the processes in porous cathodes of different geometry. The macroscopic shape of an electrode seems to be of great significance for the characteristics of the system, particularly when determining the maximum discharge current at a fixed value of electrode efficiency. This can be explained by the changes in the formation conditions of a depleted electrolyte region remote from the electrode surface.

On the basis of the model put forward, we also explained the deviation (of no less than an order of magnitude) between the theoretically predicted [2] and typical experimental values of discharge currents. The lithium-battery model seems to be quite efficient, and the results of calculations on its basis adequately conform with experiments. It is predicted that the way to enhance the operational efficiency of lithium batteries lies in the use of porous cathodes.

For porous materials, the porosity coefficient $P$ is the additional macrocharacteristic that is determined by the number of pores in the ingot bulk. The liquid porosity is of real importance, i.e., the volume of pores that have an outlet to the electrode surface. These pores play the major role in the transport of ions. The model takes into account the physical parameters of electrode materials such as the diffusion coefficient $D$ and the saturating concentration $c_{01}$ for ions diffusing from the electrolyte to the electrode. The electrolyte is characterized by the initial concentration of ions $c_{01}$. The concentrations of ions of opposite sign are assumed equal, i.e., the electroneutrality is retained. The diffusion coefficients for ions of corresponding sign are equal to $D$, and $D$.

It is assumed that the concentration of ions in the electrolyte $c_{z}$ is a function of a single coordinate $z$ ($0 < z < L$), i.e., the model neglects the local variations of concentration within the pores. This also means that in the two-dimensional and three-dimensional cases, the axially and spherically symmetrical solutions are considered.
In microparticles constituting the electrode, the concentration profile \( c_i(y, z) \) depends on the coordinate \( y \) (in the system of coordinates related with a microparticle, \( 0 < y < r \)) as well as on the position of a microparticle \( z \) in the coordinate system related with the macroscopic electrode. The coordinate \( z \) is the parameter the value of which is assumed constant for a given microparticle.

**INITIAL EQUATIONS**

In the electrode material, the evolution of the diffusion profile is described by Fick’s equation

\[
\frac{\partial c_i(y, z)}{\partial t} = \nabla_y D_y \nabla_y c_i(y, z),
\]

where \( \nabla_y \) is an operator in the coordinate system used for describing the processes within a microparticle. The boundary conditions for the gradients of concentration are

\[
\nabla_y c_i(y, z) \big|_{y = 0} = 0,
\]

\[
\nabla_y c_i(y, z) \big|_{y = r} = -i(y, z)/(FD_y).
\]

Boundary conditions (2) at the outer boundary of the electrode microparticle are connected with the current density \( i \) of the ion transport across the microparticle surface.

The transport equations in the electrolyte should take into account both the ion flow to the electrode and the variations in the electrical potential \( \Phi \). The system of equations for determination of \( c_i(z) \) has the following form:

\[
\frac{\partial c_i(z)}{\partial t} = \nabla_z D_z \nabla_z [c_i(z) \nabla_z \Phi(z)F/(RT)],
\]

where \( F \) is the Faraday number, \( R \) is the Rydberg constant, \( T \) is the temperature, \( g = n_e (1 - P)/(r \Delta P) \) is the geometric factor whose value is determined by the total surface of microparticles in a volume unit, and \( n_e \) is the factor determined by the geometry of microparticles and is equal to 1 for planar particles, 2 for cylinders, and 3 for spheres.

The boundary conditions at the bottom of a pore \( (z = 0) \) and at the electrode surface \( (z = L) \) have the following form:

\[
\frac{\partial c_i}{\partial z} \big|_{z = 0} = \frac{\partial \Phi}{\partial z} \big|_{z = 0} = 0,
\]

\[
c_i(L) = c_{i0}, \quad \Phi(L) = \Phi_1,
\]

where \( \Phi_1 \) is a temporal function chosen in such a way as to ensure a constant total current through the cell.

To relate the concentrations of ions in the electrode and electrolyte with the potential in this region, we use a model that takes into account the interaction between the ions diffusing into the electrode matrix [2]:

\[
c_i(z) = \frac{(c_{i0} - c_i(z))}{c_{i0} - c(r, z)} \times \exp\left(\frac{c_i(z)}{\Phi(z) - \Pi + f(-0.5 + c_i(z)/c_{i0})} F/(RT)\right),
\]

where \( f \) and \( \Pi \) are the constants characterizing the electrode material. In further numerical calculations, we assume \( f = 16.2 \) V and \( \Pi = 2.17 \) V. Equation (5) makes it possible to express the potential as a function of concentrations

\[
\Phi(z) = \Pi + (RT/F) \left(\ln((c_{i0} - c_i(z))/c_i(z)) + \ln(c_i(z)) + f(c_i(z)/c_{i0} - 0.5)\right).
\]

For the system of equations (1)–(5), numerical solutions are found simulating the processes taking place in real time. Situations are possible when we can introduce additional simplifications into the model for important parameters values. In the one-dimensional case, this system coincides with that considered in [2].

**MODEL SYSTEM**

We transform the initial system of equations (1)–(5) into a dimensionless form. In this case, the dimensionless variables of the time \( \tau = (D_y/r^2) \), the coordinates inside an electrode microparticle \( Y = y/r \), and the coordinates of the electrode as a whole \( Z = z/L \) appear, i.e., in fact, two length scales are used.

The most general approach to numerical simulation presupposes solving a single diffusion equation for the electrolyte and \( N \) diffusion equations for electrode microparticles at different distances from the pore bottom, where \( N \) is the parameter of the discreteness of the numerical model. The volume of calculations can be substantially reduced by taking into account the nature of real processes and the parameters of the system. At the diffusion coefficients \( D_y \) from \( 10^{-9} \) to \( 10^{-8} \) cm\(^2\)/s, \( D_z = 1.61 \times 10^{-6} \) cm\(^2\)/s and \( D_x = 6.45 \times 10^{-6} \) cm\(^2\)/s [2–5] and geometrical parameters \( L = 0.05 \) cm and \( r = 0.5–2 \) \( \mu \)m, the dimensionless diffusion coefficient

\[
U_{\ast, \ast} = (D_{\ast, \ast}/D_y)(r/L)^2
\]

for the electrolyte proves to be substantially smaller than 1. This means that the diffusion processes within microparticles are completed considerably more rapidly than those in the electrolyte, despite the fact that \( D_{\ast, \ast} \gg D_y \). This makes it possible to assume that the concentration of the substance diffusing within a microparticle is constant. In this case, the geometrical parameters of microparticles and the electrode as a whole are of great significance.

The equations of the processes in electrolyte take the form

\[
\frac{\partial c(Z)}{\partial \tau} = \nabla_Z U_c(\nabla_Z c(Z) + c(Z) \nabla_Z E(Z)),
\]

\[
\frac{\partial c(Z)}{\partial \tau} = \nabla_Z U_s(\nabla_Z c(Z) - c(Z) \nabla_Z E(Z)) + J(Z) G,
\]
where \( c(Z) = c_0(Z)/c_{00} \), \( E = (\Pi - \Phi)F/(RT) \), \( G = (1 - \delta)c_{00}/(Pc_{00}) \) is a geometrical factor, and \( J(Z) = irn_0/(Fc_{00}D_e) \) is the dimensionless density of the ion flow penetrating into the electrode from the electrolyte.

The expression for the potential in the dimensionless form is

\[
E = \ln\left(\frac{1 - X(1, Z)}{X(1, Z)}\right) + \ln(c(Z)) + f(X(1, Z) - 0.5),
\]

where \( X = c_0/Z_{00} \) is the dimensionless concentration at the electrode surface, which in further calculations is assumed independent of the coordinate \( Y \). Boundary conditions (4) take the following form:

\[
\begin{align*}
\frac{\partial c}{\partial Z}|_{Z=0} &= \frac{\partial E}{\partial Z}|_{Z=0} = 0, \\
c(z = 1) &= 1; \quad E(Z = 1) = E_1,
\end{align*}
\]

where \( E_1 \) is the potential difference between the electrode and the electrolyte at the pore’s immediate edge. This value can be controlled by the parameters of the external circuit.

After composing the difference of equations (8) and (9) and using the expression for potential (10), we obtain equations for \( c(Z) \) and \( X(Z) \) that have the form of diffusion equations with complex sources and effective diffusion coefficients:

\[
\begin{align*}
\frac{\partial c(Z)}{\partial \tau} &= U_c(2\frac{\partial c(Z)}{\partial Z} - A\frac{\partial^2 X(Z)}{\partial Z^2} - B\frac{\partial X(Z)}{\partial Z}) \\
-4\frac{\partial^2 X(Z)}{\partial Z^2} - B\frac{\partial X(Z)}{\partial Z},
\end{align*}
\]

where \( D_1 = 1, 2, \) and \( 3 \) for planar, cylindrical, and spherical geometries. The higher curves of the profiles of lithium concentration in the electrode correspond to a later stage of the process. The corresponding filling degrees of the electrode are 4.4, 15, 30, 50, and 81%.

The problem to be solved in simulating is to achieve the maximum discharge current using the electrode volume to the fullest possible extent. When solving numerically the system of equations, the amount of lithium ions diffused into the electrode was determined at every step. The difference with the current value at the previous step was eliminated by changing the potential difference between the electrode and the electrolyte directly at the electrode surface. The significant factor under those conditions is the formation of a region far removed from the external electrode surface and depleted of Li⁺ ions, which leads to the actual exclusion of a part of the electrode volume from the process. It eventually becomes impossible to use the battery as a result of an intolerable decrease in the potential difference.

Figure 1 shows the results of calculations of concentration profiles of lithium ions in the electrode and the electrolyte at different stages of the process in cathodic material with the porosity \( \rho = 0.2 \). These curves correspond to the density of the maximum discharge current: 3.43 mAh/cm² (34.3 mAh/cm³). The value in the brackets is the current value per volume unit of the electrode, which allows one to compare electrodes with different geometries. The higher curves of the profiles of lithium concentration in the electrode correspond to a later stage of the process. The corresponding filling degrees of the electrode are 4.4, 15, 30, 50, and 81%.

Among the set of profiles of the lithium-cation concentration in the electrolyte, the lower curves correspond to a higher degree of battery discharge.

At an increase in electrode thickness, the value of the maximum discharge current sharply decreases, for example, at \( L = 0.2 \) cm, the current is 2.14 mAh/cm³.

Figure 2 shows the potential difference of this process as a function of the filling degree of the electrode. For comparison, we show the potential difference plot for a quasi-equilibrium case (small discharge currents).

The transport of lithium into the electrode bulk proceeds mainly along the pores; therefore, it is easy to explain the dependence of the maximum discharge current on the porosity coefficient. Note that the typical experimental value of 0.2 mAh/cm² (see [4]) is substantially lower than that obtained in this work (3.43 mAh/cm³). The deviation observed can be explained by the com-
plex, irregular structure of pores, although all pores in the model studied were considered as the most effective channels for lithium transport. The decrease in the maximum current as compared with the upper estimate obtained above is explained by the tortuosity and corrugation of the pores, as well as by the presence of hollows poorly connected with the surface. We can take into account the listed factors by introducing the effective diffusion coefficient \( D_{+,-,\text{ef}} \). The value of the discharge current is approximately proportional to the value of the diffusion coefficient \( D_{+,-,\text{ef}} \):

\[
D_{+,-,\text{ef}} = KD_{+,-}.
\]

To determine the values of the coefficient \( K \), we can use the results of model experiments on the conductivity \( \chi \) of the electrolyte that fills the porous sample. Experiments [8] showed the nonlinear nature of the dependence of conductivity on the electrolyte amount. Practically all experimental points lie between the curves

\[
\frac{\chi_{\text{exp}}}{\chi_0} = bS^3
\]

Fig. 1. (1) Lithium concentration distribution in a plane electrode \( L = 0.05 \text{ cm} \), (2) concentration profiles of \( \text{Li}^+ \) in electrolyte. \( P = 0.2 \), the discharge current is 3.43 mA/cm\(^2\). The electrode efficiency is 90% at the potential-difference drop from 2.45 to 1.86 V. See explanations in text.

Fig. 2. (1) The potential difference for a planar electrode at the discharge current of 3.43 mA/cm\(^2\), (2) the potential difference at a small discharge current as a percentage function of the electrode efficiency.

Fig. 3. (1) The distribution of lithium concentration in a cylindrical electrode of a 0.05-cm radius; (2) the concentration of \( \text{Li}^+ \) in electrolyte; \( P = 0.2 \); the discharge current is 183 mA/cm\(^3\). The electrode efficiency is 95%. See explanations in text.

Fig. 4. (1) The distribution of lithium concentration in a spherical electrode \( L = 0.05 \text{ cm} \), (2) the concentration of \( \text{Li}^+ \) in electrolyte; \( P = 0.2 \); the discharge current is 376 mA/cm\(^3\). See explanations in text.
at $b = 0.5$ and $2$, where $S$ is a fraction of the electrode volume occupied by electrolyte and $\chi_0$ and $\chi_{\text{exp}}$ are the electrolyte conductivity and the experimental value of the electrode conductivity, respectively.

At the porosity $P = 0.2$, the value $K = bS^2$, which determines the renormalization of the diffusion coefficient, lies in the interval of $0.02$–$0.08$, and the value of the maximum discharge current lies in the interval from 0.07 to 0.28 mA/cm$^2$, which agrees with the experiment.

The results of simulation for axially symmetrical and spherically symmetrical electrodes are shown in Fig. 3 (current, 183 mA/cm$^2$; filling degree: 20, 50, 80%) and Fig. 4 (current, 376 mA/cm$^3$; filling degree: 7.5, 50, 75, and 90%).

There are at least two reasons for the substantial increase in the maximum discharge current at the changeover from one-dimensional to two-dimensional and three-dimensional cases: the increase in the ratio between the surface in contact with the electrolyte and the electrode volume, and also the less favorable conditions for formation of the depleted region in the electrolyte, and thus, the fuller use of the electrode.

The calculations carried out show the important role of geometrical factors in the optimization of the design of lithium batteries. Not only the electrode porosity but also the geometry of the macroscopic electrode is important, and a planar electrode is the least effective for achieving a high discharge current.

REFERENCES