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Вплив пористості на продуктивність літійової батареї з мікропористим вуглецевим електродом

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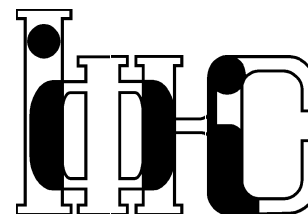
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Dmitry Portnyagin

EFFECT OF POROSITY ON THE PERFORMANCE OF
LITHIUM BATTERY WITH MICROPOROUS CARBON
ELECTRODE

ЛЬВІВ

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Вплив пористості на продуктивність літієвої батареї з мікропористим вуглецевим електродом

Д.В. Портнягін

Анотація. Чисельно моделювалася розрядка літієвої батареї із мікропористим вуглецевим електродом в режимі заданого струму при різних значеннях пористості електроду. При цьому досліджувався вплив пористості на продуктивність комірки. Отримані результати свідчать про те, що існує оптимальне значення пористості, яке відповідає максимальній продуктивності.

Effect of porosity on the performance of lithium battery with microporous carbon electrode

D.V. Portnyagin

Abstract. Discharge of lithium cell with microporous carbon electrode under galvanostatic control at several values of the porosity of electrode has been modelled to study the impact of the porosity on performance of the cell. The obtained results testify that there is an optimal porosity corresponding to maximal performance.

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1. Introduction.

Lithium ion battery with microporous electrode proved to be a reliable high energy density source of energy in mobile phones, laptop computers, other portable devices and electric vehicles the demand for which has sprung in the market in recent years. Lithium serves as a cathode material because of its low electronegativity. Porous materials are used for anode due to their large surface area associated with high energy storage.

Simulation of charge/discharge processes can help to gain a deeper insight into the nature of the phenomena that occur during the operation of these devices. This also allows to optimize the battery to obtain a higher performance. Recently the simulation of the intercalation of lithium into the structure of porous electrode has been attracting the attention of several authors [3], [1], [5]. In these papers diffusion is considered as the main driving force during the operation of the battery and the transport of lithium ions through the porous electrode is governed by Fick's second law.

In the present paper we calculated numerically the performance of the cell at different values of the porosity of anode and separator. The results confirms that the performance increases with the porosity of separator, while there exists optimal porosity of anode.

2. Basic considerations.

We study the galvanostatic discharge of lithium battery at different values of the porosity of electrode and separator. In our research we heavily rely upon the data from [1]. The battery consists of lithium foil, porous separator of thickness $L_s = 25\mu m$, porous carbon electrode of thickness $L_1 = 125\mu m$ made of cylindrical particles of radius $R_s = 3,5\mu m$, and current collector. The battery is immersed in 1M solution of LiClO_4 in propylene carbonate.

The battery is discharged from its initial state with $U_0 = 0.91489V$ to $0.01V$ cutoff voltage at current density $12.05A/m^2$.

During the discharge of the battery, lithium is dissolved into lithium ions from the negative electrode, migrates through the separator and finally intercalates into the carbon electrode. During the charge the reverse process takes place. We neglect the electrodes expansion and contraction. Verbrugge and Koch [6] considered the gradient of the chemical potential of the inserted lithium ions as the driving force.

We consider cylindrical particles with the ratio of length to radius

sufficiently large, for which the concentration of lithium inside the particle is a function only of radial distance, governed by the equation

$$\frac{\partial y}{\partial \tau} = \frac{1}{R} \frac{\partial}{\partial R} \left(R f \frac{\partial y}{\partial R} \right) \quad (2.1)$$

$$y = y_0, \quad \text{at } \tau = 0, \forall R; \quad (2.2)$$

$$\frac{\partial y}{\partial R} = 0 \quad \text{at } R = 0, \forall \tau; \quad (2.3)$$

$$\frac{\partial y}{\partial R} = -\frac{j_n^+}{D_s C_{s,max}} \frac{R_s}{f} \quad \text{at } R = 1, \forall \tau; \quad (2.4)$$

where $\tau = tD_s/R_s^2$, $y = C_s/C_{s,max}$, $R = r/R_s$; are dimensionless variables. D_s is the diffusion coefficient in the solid phase, assumed to be constant, R_s is the radius of the particle, C_s is the concentration of lithium ions inside the particle, $C_{s,max}$ is the maximum concentration of lithium ions inside the particle, f is the activity factor dependant on the intercalation fraction and calculated by Verbrugge and Koch [6], j_n^+ is the flux of lithium ions at the surface of the particle. The initial value of y is equal to 0.01. The flux of lithium ions at the surface of the particle is equal to the electrochemical reaction rate per unit of surface area of the particle as given by a Butler-Volmer reaction rate expression

$$j_n^+ = K (C(1 - y|_{R=1}))^{\beta-1} (y|_{R=1})^\beta \left\{ \exp \left[\frac{(1-\beta)F}{\Re T} (U_{app} - U) \right] - \exp \left[\frac{-\beta F}{\Re T} (U_{app} - U) \right] \right\},$$

where C is the concentration of the electrolyte, K is the reaction rate constant ($K = k_c^{1-\beta} k_a^\beta$), F is the Faraday constant, \Re is universal gas constant, T is temperature, η is the potential between solid phase and electrolyte, and U represents the open-circuit cell potential with respect to a metallic lithium electrode which is evaluated at the surface of the particle where the electrochemical reaction takes place and which is given by

$$U = U_s + \frac{\Re T}{F} \ln \left(\frac{1 - y|_{R=1}}{y|_{R=1}} \right) - \sum_{s=2}^7 \frac{\Omega_s}{F} s (y|_{R=1})^{s-1} \quad \text{for } 0 < y|_{R=1} < 0.985, \quad (2.5)$$

where U_s is the standard cell potential with respect to a metallic lithium electrode, and Ω_s are the self-interaction energies. The material of which

is made carbon electrode is not well-ordered, so the open-circuit potential does not exhibit plateaus or phase changes. We take the activity coefficient

$$f = \left(1 + \frac{d \ln \gamma_+}{d \ln y} \right) = 1 + \sum_{s=2}^7 \frac{\Omega_s}{\Re T} s (s-1) (y^{s-1} - y^s) \quad (2.6)$$

(at low lithium concentrations f increases with increasing the lithium ion concentration due to repulsive effects, takes on its maximum at $y = 0.2$, and decreases with increasing the lithium ion concentration due to low ion mobility at higher concentrations). We also add the current coursed by electric field to the righthand side of equation (2.1).

$$\frac{\partial y}{\partial t} = \frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{D_s}{R_s^2} f \frac{\partial y}{\partial R} \right) - \frac{1}{FC_{max,s}} \text{div}(\sigma E), \quad (2.7)$$

where E is the electric field, σ the ionic conductivity given by Einstein relation

$$\sigma = y C_{max,s} N_a D_s e^2 / kT,$$

k is Boltzman constant, e is elementary charge, N_a is Avogadro number.

In the first approximation we assume that the current of positive ions through the surface of the particle is entirely due to the uniform distribution within the particle of negative charge, which carbon, being more electronegative, draws from lithium, and the distribution of charge caused by imposed external electric field. However, X-ray photoelectron spectroscopy (XPS) proved [4] that after insertion the lithium retains only a fraction of the positive charge $+\delta$, while the carbon takes a negative charge $-\delta$. Therefore to the distribution of charge in the bulk of the particle we add the term associated with the nonuniform distribution of lithium ions. This results in

$$\text{div}(E) = \frac{2}{R_s \sigma_{eff,1}} j_n^+ - \delta \frac{FC_{max,s}}{\varepsilon_0} (y_{avr} - y),$$

where $\sigma_{eff,1}$ is the effective conductivity of electrolyte in the carbon

electrode, ε_0 is the dielectric constant, $y_{avr} = \int y dV / V = 2 \int_0^1 y R dR$ (or

$= 3 \int_0^1 y R^2 dR$ for spherical particles) is the average concentration of ions

in the particle, δ is the delocalization factor which equals 1 when we have naked lithium ions and negative charge, drawn from lithium, uniformly spread over carbon sites, and equals 0 when negative charge is maximally localized on lithium ions.

The ionic current across the carbon electrode i_2 is equal to the external current through the battery i_{app} at the contact with separator, and is zero at current collector. Between these two values the current is assumed to be distributed according to the equation:

$$\frac{\partial i}{\partial x} = aFj_n^+,$$

where a is the interfacial area of particles per unit volume of porous electrode, calculated by

$$a = 0.03 \cdot 2(1 - \epsilon_1)/Rs,$$

ϵ_1 - porosity of carbon electrode (ϵ_s - correspondingly the porosity of separator). It appears quite obvious that after we have pressed and baked the carbon material, only a fraction of the particle's surface will be exposed to electrolyte, so we have introduced a suitable factor in the formula for the interfacial area. These factors are chosen such in order to match the experimental values of currents on cyclic voltammograms. The equation for the concentration of the electrolyte in the solution phase of the carbon electrode is

$$\epsilon_l \frac{\partial C}{\partial t} = \nabla (\epsilon_l D_{eff,l} \nabla C) + a(1 - t_+^0)j_n^+,$$

where $l = 1, s$ (1 corresponds to electrode, s to separator), t_+^0 is transfer number, $D_{eff,l} = \epsilon_l^{0.5} D$, D is the diffusion coefficient of electrolyte, $C_{initial} = 1000 \text{ mol/m}^3$. We impose on C the following boundary conditions: (i) that the flux of ions at lithium electrode is equal to the applied current through the cell

$$\epsilon_s D_{eff,s} \nabla C|_{x=0} = i_{app}/F,$$

(ii) that the flux of mass is continuous at the separator-electrode interface

$$\epsilon_s D_{eff,s} \nabla C|_{x=L_s-0} = \epsilon_1 D_{eff,1} \nabla C|_{x=L_s+0},$$

and (iii) that its's equal to zero at current collector

$$\epsilon_1 D_{eff,1} \nabla C|_{x=L_s+L_1} = 0.$$

The potential in the solution phase is

$$\nabla \phi_1 = -\frac{i_2}{\sigma_{eff,l}} + \frac{\Re T(1 - t_+^0)}{FC} \nabla C,$$

where $\sigma_{eff,l}$, $l = \{1, s\}$ is the effective conductivity of electrolyte given in Table I.

Table I. Standard cell potential, interaction energies, model parameters for the carbon-lithium cella and physical constants.

Parameter	Value
U_0	0.91489 V
U_s	0.8170 V
Ω_2/F	0.9926 V
Ω_3/F	0.8981 V
Ω_4/F	-5.630 V
Ω_5/F	8.585 V
Ω_6/F	-5.784 V
Ω_7/F	1.468 V
$C_{s,max}$	18,000 mol/m ³
β	0.5
K	$3.28 \times 10^{-6} \text{ mol}^{1/2}/\text{m}^{1/2}s$
K_{Li}	$4.1 \times 10^{-6} \text{ mol}^{1/2}/\text{m}^{1/2}s$
$C_{initial}$	1000 mol/m ³
$T_{initial}$	298 K
$y_{initial}$	0.01
D	$2.6 \times 10^{-10} \text{ m}^2/s$
D_s	$1.0 \times 10^{-14} \text{ m}^2/s$
t_+^0	0.2
$\sigma_{eff,l}$	$\epsilon_l^{1.5} C^{0.855} (0.00179 \exp(-0.08(0.00083C - 0.6616)^2 - 0.0010733C + 0.855)) + 0.0001$
σ_{el}	100 S/m
R_s	$3.5 \times 10^{-6} \text{ m}$
L_s	$25 \times 10^{-6} \text{ m}$
L_1	$125 \times 10^{-6} \text{ m}$
k	$1.381 \times 10^{-23} \text{ J/K}$
N_a	$6.022 \times 10^{23} \text{ mol}^{-1}$
\Re	8.314 J/(mol · K)
F	96,487 C/mol
ϵ_0	$8.854 \times 10^{-12} \text{ C}^2/(N \cdot \text{m}^2)$
e	$1.9 \times 10^{-19} \text{ C}$
δ	10^{-9}

The potential in the solid phase of the electrode is

$$\nabla\phi_2 = -\frac{(i_{app} - i_2)}{\sigma_{eff}},$$

where $\sigma_{eff} = \epsilon_1^{1.5}\sigma$ is the effective conductivity of electrode. The local surface overpotential is given by

$$\eta = \phi_1 - \phi_2.$$

The total voltage of the cell is related to η by

$$V_{total} = \eta|_{x=0} + (\phi_1 - \phi_2)_{kin} - \int_{x=L_s}^{x=L_s+L_1} \frac{[i_{app} - i_2(x)]}{\sigma_{eff}},$$

where $(\phi_1 - \phi_2)_{kin}$ is given by kinetic expression

$$i_{app} = FK_{Li}C^{0.5}(\exp((0.5F/(\mathcal{R}T))(\phi_1 - \phi_2)) - \exp(-(0.5F/(\mathcal{R}T))(\phi_1 - \phi_2)))$$

with K_{Li} - the reaction rate constant at the lithium electrode.

The utilization of the cell u is defined by

$$u = (2/L_1) \int_{x=L_s}^{x=L_s+L_1} dx \int_{R=0}^{R=1} yRdR.$$

All the parameters of the cell are evaluated at $T_{initial} = 298K$ for the reasons explained in [2]. The values of the standard cell potential, the self-interaction energies, and the kinetic parameters are given in Table I.

The corresponding set of equations from Table II has been solved numerically.

At small values of the porosity of electrode the large amount of carbon material sucks out all of the lithium ions from electrolyte, as one can see from Figure 1, and new ions don't manage to be supplied quickly from the lithium foil due to small value of the effective diffusion coefficient in this case. This corresponds to the smaller overall value of the electrolyte concentration in carbon electrode. As is seen from the Butler-Volmer expression, the total current through the cell being given, the drop in cell voltage at a given instant of time must be larger to compensate for this decrease of concentration. This correspond to the battery's running

for smaller period of time and to lower performance (as the exponent of performance we have chosen the value of utilization at cut-off voltage 0.01V).

At the same time at large values of the porosity of electrode the small amount of carbon material corresponds to small interfacial area in this case. The Butler-Volmer expression shows that this, the total current through the cell being given, makes the current across each particle large and the drop in cell voltage at a given instant of time must be large in this case. Thus this results in the battery's running for small period of time and in low performance.

The total performance of the cell is the result of interplay these two aforementioned competing factors. On the one hand the larger porosity of electrode promotes the more rapid discharge of the cell, on the other hampers it. Since the performance is small for both large and small values of porosity due to different reasons, one could think (see Figure 2) that there must exist some optimal value of porosity of electrode giving the maximal performance of the battery. Figure 3 verifies this point.

The increase in the porosity of separator, as should be expected, positively affects the performance of the battery. Larger values of the porosity of separator promote the transport of lithium ions from lithium foil across the battery to the carbon electrode, which results in larger overall values of concentration of electrolyte in carbon electrode. Figure 4, which shows the dependence of the performance of the cell on the porosity of separator, confirms this.

Table II. System of model equations and boundary conditions.

Region	Value	Equation or boundary condition
$x = 0$	y	$y = 0$
	C	$\epsilon_s D_{eff,s} \nabla C = i_{app}/F$
	i_2	$i_2 = i_{app}$
$0 < x < L_s$	y	$y = 0$
	C	$\epsilon_s \frac{\partial C}{\partial t} = \nabla (\epsilon_s D_{eff,s} \nabla C)$
	i_2	$i_2 = i_{app}$
	η	$\nabla \eta = \frac{i_2}{\sigma_{eff,s}} - \frac{\Re T(1 - t_+^0)}{FC} \nabla C$
$x = L_s$	C	$\epsilon_s D_{eff,s} \nabla C _{L_s-0} = \epsilon_1 D_{eff,1} \nabla C _{L_s+0}$
$L_s < x < L_s + L_1$	y	(2.7) with (2.2)-(2.4);
	C	$\epsilon_1 \frac{\partial C}{\partial t} = \nabla (\epsilon_1 D_{eff,1} \nabla C) + a(1 - t_+^0) j_n^+$
	i_2	$\nabla i_2 = a F j_n^+$
	η	$\nabla \eta = \frac{-i_{app}}{\sigma_{eff}} + i_2 \left(\frac{1}{\sigma_{eff}} + \frac{1}{\sigma_{eff,1}} \right) - \frac{\Re T(1 - t_+^0)}{FC} \nabla C$
$x = L_s + L_1$	C	$\epsilon_1 D_{eff,1} \nabla C = 0$
	i_2	$i_2 = 0$

3. Conclusions.

We have made a simulation of the discharge of lithium cell with micro-porous carbon electrode under galvanostatic control at different values of the porosity of electrode and separator. Two competing factors play role in the discharge. The one increases with the value of the porosity of carbon electrode, the other decreases. There is an optimal value of the porosity of carbon electrode that gives the maximal performance. The performance of the battery increases with the porosity of separator.

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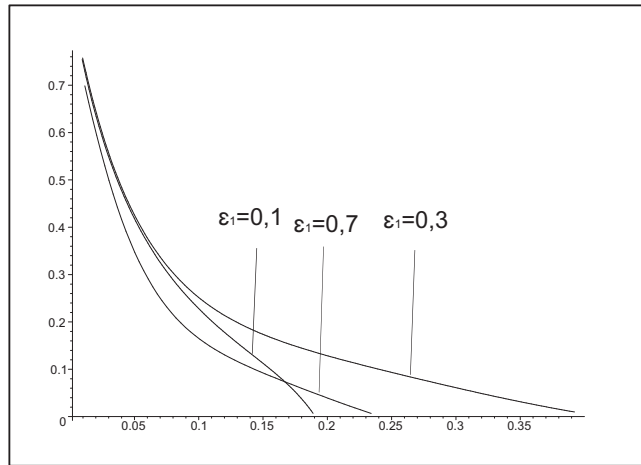


Figure 1. Cell voltage (V) vs. utilization at the values of the porosity of carbon electrode $\varepsilon_1 = 0.1$, $\varepsilon_1 = 0.3$ and $\varepsilon_1 = 0.7$ the porosity of separator $\varepsilon_s = 0.55$.

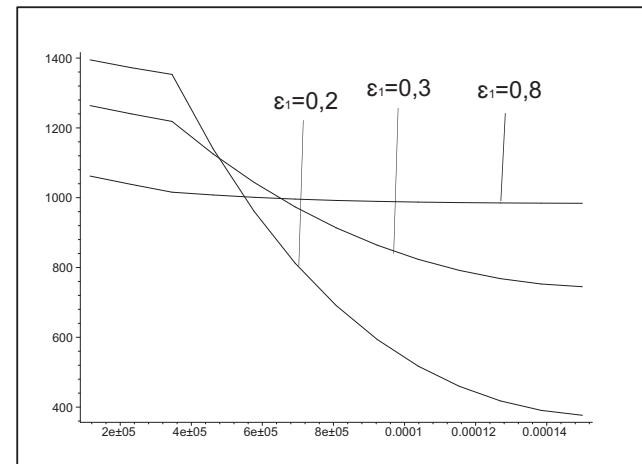


Figure 2. Concentration of the electrolyte vs. distance across the cell at the values of the porosity of carbon electrode $\varepsilon_1 = 0.2$, $\varepsilon_1 = 0.3$ and $\varepsilon_1 = 0.8$ and the porosity of separator $\varepsilon_s = 0.55$.

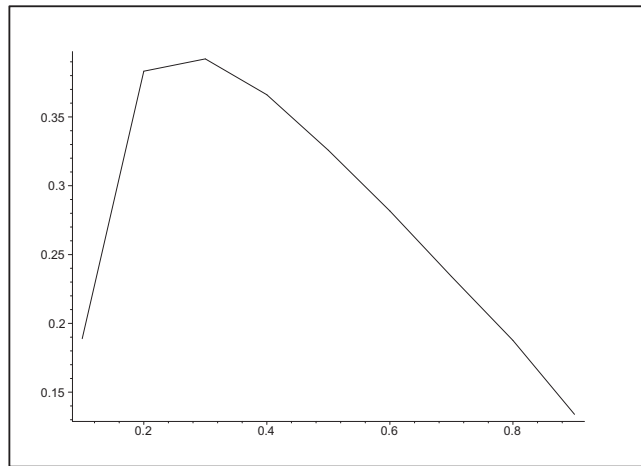


Figure 3. Performance of the cell (utilization at 0.01V) vs. porosity of carbon electrode at the value of the porosity of separator $\varepsilon_s = 0.55$.

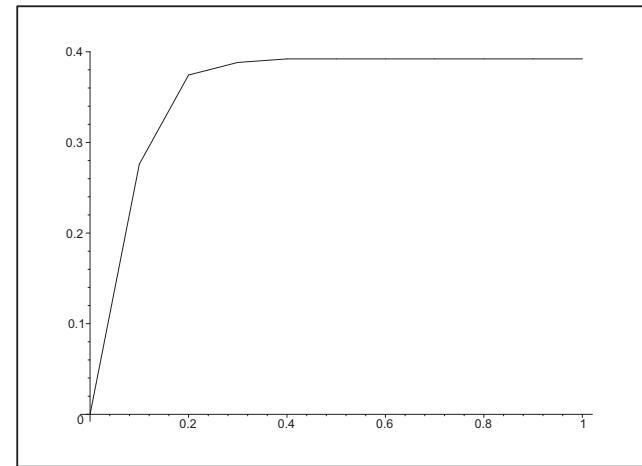


Figure 4. Performance of the cell (utilization at 0.01V) vs. porosity of separator at the value of the porosity of carbon electrode $\varepsilon_1 = 0.3$.