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ЧИСЕЛЬНЕ МОДЕЛЮВАННЯ РОЗРЯДКИ ЛІТІЄВОЇ БАТАРЕЇ З  $Bi_2Se_3$  ПОРОШКОПОДІБНИМ ЕЛЕКТРОДОМ

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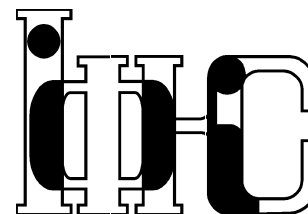
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SIMULATION OF DISCHARGE OF LITHIUM BATTERY WITH  
 $Bi_2Se_3$  POWDERED ELECTRODE

ЛЬВІВ

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### Чисельне моделювання розрядки літієвої батареї з $Bi_2Se_3$ порошкоподібним електродом

Д.В. Портнягін

**Анотація.** Моделювалася циклічна зарядка-розрядка та розрядка літієвої батареї із  $Bi_2Se_3$  порошкоподібним електродом в режимі заданої напруги та заданого струму. Для повної моделі було отримано циклічні вольтамперні характеристики та розрядні криві, типові для двофазної системи. Досліджувався вплив пористості на продуктивність комірки. Отримані результати свідчать про те, що існує оптимальне значення пористості, яке відповідає максимальній продуктивності.

### Simulation of discharge of lithium battery with $Bi_2Se_3$ powdered electrode

D.V. Portnyagin

**Abstract.** Cycling under potentiodynamic control and galvanostatic discharge of lithium cell with  $Bi_2Se_3$  powdered electrode has been modelled. Cyclic voltammograms and discharge curves typical to the two-phase system in a complete model have been obtained. Galvanostatic discharge 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.

We have made a comparison of the predictions of the model at different scan rates and different discharge currents, and obtained cyclic voltammograms and discharge curves, typical to the two-phase system.

We calculated numerically the performance of the cell at different values of the porosity of anode. The results confirms that there exists optimal porosity of anode.

## 2. Basic considerations.

We study the cycling under potentiodynamic control and galvanostatic discharge of lithium battery. The battery consists of lithium foil of thickness  $L_{Li} = 0,55mm$ , porous separator of thickness  $L_s = 100\mu m$ ,  $Bi_2Se_3$  powder electrode of thickness  $L = 0,55mm$  made of spherical particles of radius  $R_s = 50\mu m$ , and current collector, and has the form of a cylinder with high  $H = L_{Li} + L_s + L_1$  and radius of the base  $R_c = 10mm$ . The battery is immersed in 1M solution of  $LiClO_4$  in propylene carbonate.

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 anode. During the charge the reverse process takes place. We assume that the intercalation of lithium ions into anode continues until the concentration of intercalated ions in anode reaches the value of that of solid lithium, which is associated with the formation of film of pure lithium.

The concentration of lithium inside the particle is a function only of radial distance, governed by the equation

$$\frac{\partial y}{\partial t} = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{D_s}{R_s^2} \frac{\partial y}{\partial R} \right) \quad (2.1)$$

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

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

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

where  $t$  is time,  $y = C_s/C_{s,max}$ ,  $R = r/R_s$ ; are dimensionless variables.  $D_s$  is the diffusion coefficient in the solid phase,  $R_s$  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,  $j_n^+$  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,  $\eta$  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

$$U = \sum_{m=0}^5 U_m (y|_{R=1})^m \quad \text{for } 0 < y|_{R=1} < 1.$$

We take the diffusion coefficient

$$D_s = \sum_{m=0}^5 D_m y^m \quad (2.5)$$

The formulas for the open-circuit potential and the diffusion coefficient have been obtained by means of least square regression of experimental graphs.

We add the current coursed by electric field to the righthand side of equation (2.1).

$$\frac{\partial y}{\partial t} = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{D_s}{R_s^2} \frac{\partial y}{\partial R} \right) - \frac{1}{FC_{max,s}} \text{div}(\sigma E), \quad (2.6)$$

where  $E$  is the electric field,  $\sigma$  the ionic conductivity given by Einstein relation

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

$k$  is Boltzman constant,  $e$  is elementary charge,  $N_a$  is Avogadro number,  $\bar{D}_s$  is the average diffusion coefficient.

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  $Bi_2Se_3$ , 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 anode material 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

$$\text{div}(E) = \frac{3}{R_s \sigma_{eff,el}} j_n^+ - \delta \frac{FC_{max,s}}{\varepsilon_0} (y_{avr} - y),$$

where  $\sigma_{eff,el}$  is the effective conductivity of electrolyte,  $\varepsilon_0$  is the dielectric constant,  $y_{avr} = \int y dV / V = 3 \int_0^1 y R^2 dR$  is the average concentration of ions in the particle,  $\delta$  is the delocalization factor which equals 1 when we have naked lithium ions and negative charge, drawn from lithium, uniformly spread over  $Bi_2Se_3$  sites, and equals 0 when negative charge is maximally localized on lithium ions.

The ionic current across the anode,  $i_2$  is equal to the external current through the battery  $i_{total}$  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:

$$\frac{\partial i_2}{\partial x} = a F j_n^+,$$

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

$$a = 0.02 \cdot 3(1 - \epsilon)/Rs$$

$\epsilon$  - porosity. It appears quite obvious that after we have pressed and baked the  $Bi_2Se_3$  powder, 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. The equation for the concentration of the electrolyte in the solution phase of the carbon electrode is

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

where  $t_+^0$  is transfer number,  $D_{eff} = \epsilon^{0.5} D$ ,  $D$  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 total current through the cell

$$\epsilon D_{eff} \nabla C|_{x=L_s+L_1} = i_{total}/F,$$

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

$$\epsilon D_{eff} \nabla C|_{x=0} = 0.$$

The potential in the solution phase is

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

where  $\sigma_{eff,el}$  is the effective conductivity of electrolyte given in Table I. The potential in the solid phase of the electrode is

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

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

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

The total voltage of the cell is related to  $\eta$  by

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

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

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

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

All the parameters of the cell are evaluated at  $T=298K$  for the reasons explained in [2]. The values of the coefficients in the expression for open-circuit potential, the diffusion coefficient, and the kinetic parameters are given in Table I.

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

### 3. Cyclic Voltammograms.

The applied potential is changed linearly with time and is given by

$$U_{app} = U_{ini} + \omega t$$

where  $U_{ini}$  is the initial applied potential,  $\omega$  is the sweep rate,  $t$  is time. At a sweep rates 1, 2 and 5 mV/s the battery was discharged from its initial state to 1.2V, then it was charged to 2.5 V, after that the battery was again discharged to 1.2V. These steps were repeated twice to reach a periodic state. The periodic state is the state, at which the results are uniform and sustained during consecutive cycles, when cycled under the same conditions.

Let us clear up how the speed of changing of  $j_n^+$  during the cycling depends on the speed of changing of the applied voltage  $U_{app}$ . We have

$$\begin{aligned} \frac{d}{dt} j_n^+ &= KC^{\beta-1} [(\beta - 1) (1 - y|_{R=1}) - \beta (y|_{R=1})] \times \\ &\times ((1 - y|_{R=1}))^{\beta-2} (y|_{R=1})^{\beta-1} \left\{ \exp \left[ \frac{(1 - \beta)F}{\Re T} (U_{app} - U) \right] - \right. \\ &\quad \left. - \exp \left[ \frac{-\beta F}{\Re T} (U_{app} - U) \right] \right\} \frac{dy}{dt} + \\ &+ KC^{\beta-1} \frac{F}{\Re T} ((1 - y|_{R=1}))^{\beta-1} (y|_{R=1})^\beta \{ (1 - \beta) \times \\ &\quad \times \exp \left[ \frac{(1 - \beta)F}{\Re T} (U_{app} - U) \right] + \\ &\quad \left. + \beta \exp \left[ \frac{-\beta F}{\Re T} (U_{app} - U) \right] \right\} \left[ \frac{U_{app}}{dt} - U' \frac{dy}{dt} \right]. \end{aligned}$$

**Table I. Model parameters for the lithium cell and physical constants.**

Parameter	Value
$U_{ini}$	1.9387 V
$U_0$	1.9387 V
$U_1$	-4.2547 V
$U_2$	27.1704 V
$U_3$	-75.0395 V
$U_4$	93.1909 V
$U_5$	-43.0055 V
$D_0$	$0.1323 \times 10^{-12}$ m <sup>2</sup> /s
$D_1$	$0.1765 \times 10^{-11}$ m <sup>2</sup> /s
$D_2$	$0.1400 \times 10^{-10}$ m <sup>2</sup> /s
$D_3$	$0.3633 \times 10^{-10}$ m <sup>2</sup> /s
$D_4$	$0.3950 \times 10^{-10}$ m <sup>2</sup> /s
$D_5$	$0.1533 \times 10^{-10}$ m <sup>2</sup> /s
$C_{s,max}$	76,945 mol/m <sup>3</sup>
$\beta$	0.5
$K$	$10^{-6}$ mol <sup>1/2</sup> /m <sup>1/2</sup> s
$K_{Li}$	$4.1 \times 10^{-6}$ mol <sup>1/2</sup> /m <sup>1/2</sup> s
$C_{initial}$	1000 mol/m <sup>3</sup>
$T$	298 K
$y_{initial}$	0.01
$D$	$2.6 \times 10^{-10}$ m <sup>2</sup> /s
$t_+^0$	0.2
$\sigma_{eff,el}$	$\epsilon^{1.5} C^{0.855} (0.00179 \exp(-0.08(0.00083C - 0.6616)^2 - 0.0010733C + 0.855)) + 0.0001$
$\sigma$	20 S/m
$R_s$	$50 \times 10^{-6}$ m
$L_s$	$100 \times 10^{-6}$ m
$L_1$	$0.55 \times 10^{-3}$ m
$k$	$1.381 \times 10^{-23}$ J/K
$N_a$	$6.022 \times 10^{23}$ mol <sup>-1</sup>
$\Re$	8.314 J/(mol · K)
$F$	96,487 C/mol
$\epsilon_0$	$8.854 \times 10^{-12}$ C <sup>2</sup> /(N · m <sup>2</sup> )
$e$	$1.9 \times 10^{-19}$ C
$\delta$	$2 \times 10^{-10}$
$\epsilon$	0.7

Substituting for  $\frac{dy}{dt}$  its expression from the diffusion equation in which we neglect electrostatic interaction, and substituting 1 for  $y$  and its spacial derivatives, since they are dimensionless magnitudes, hence we get the following estimate for the order of magnitude:

$$\frac{d}{dt} j_n^+ \simeq j_n^+ \left( \sum_{m=0}^5 |D_m| \right) / R_s^2 + (\pm 1) j_n^+ \frac{F}{\Re T} \left\{ \beta \frac{U_{app}}{dt} - \beta \left( \sum_{m=0}^5 |U_m| \right) \left( \sum_{m=0}^5 |D_m| \right) / R_s^2 \right\}, \quad (3.1)$$

where we take "+" when  $j_n^+$  is positive, "-" when it is negative. Hence we can conclude that the hysteresis is the more significant, the steeper is the relation graph of  $j_n^+$  vs. applied voltage, and the stronger, in turn, is the following inequality:

$$\frac{U_{app}}{dt} \gg \frac{\Re T}{F} \left( \sum_{m=0}^5 |U_m| \right) \left( \sum_{m=0}^5 |D_m| \right) / R_s^2. \quad (3.2)$$

And vice versa, the hysteresis is the less significant, the stronger is the reverse inequality:

$$\frac{U_{app}}{dt} \ll \frac{\Re T}{F} \left( \sum_{m=0}^5 |U_m| \right) \left( \sum_{m=0}^5 |D_m| \right) / R_s^2 \quad (3.3)$$

(in this case  $\frac{d}{dt} j_n^+$  dose not become large, because the whole righthand side in (3.1) is multiplied by the derivative of  $y$  with respect to radial distance, which, the concentration profile being sloping, is small). The above said is verified by Figure 4.

The cyclic voltammograms of our battery are characterized by two peaks typical to the two-phase system, as Figures 1-3 indicate. One peak corresponds to discharge, the other - to charge. They are accounted for by the formation of double layer at the solid phase-solution interface and avalanche-like increase in the number of charge carriers. From the viewpoint of mathematical simulation they can be explained by the fact that when we move on a plateau the difference between the open-circuit potential of the battery and the applied potential, as well as the current across the surface of the particle, increases rapidly, which corresponds to the peak. At the same time, when we aren't on a plateau anymore

and the open-circuit potential begins to decrease, the aforementioned

**Table II. System of model equations and boundary conditions.**

Region	Value	Equation or boundary condition
$x = L_s + L_1$	$y$	$y = 0$
	$C$	$\epsilon D_{eff} \nabla C = i_{total}/F$
	$i_2$	$i_2 = i_{total}$
$L_s + L_1 > x > L_1$	$y$	$y = 0$
	$C$	$\epsilon \frac{\partial C}{\partial t} = \nabla (\epsilon_s D_{eff} \nabla C)$
	$i_2$	$i_2 = i_{total}$
	$\eta$	$\nabla \eta = \frac{i_2}{\sigma_{eff,el}} - \frac{\Re T(1 - t_+^0)}{FC} \nabla C$
	$\eta$	(2.6) with (2.2)-(2.4);
$L_1 > x > 0$	$C$	$\epsilon \frac{\partial C}{\partial t} = \nabla (\epsilon D_{eff} \nabla C) + a(1 - t_+^0) j_n^+$
	$i_2$	$\nabla i_2 = a F j_n^+$
	$\eta$	$\nabla \eta = \frac{-i_{total}}{\sigma_{eff}} + i_2 \left( \frac{1}{\sigma_{eff}} + \frac{1}{\sigma_{eff,1}} \right) - \frac{\Re T(1 - t_+^0)}{FC} \nabla C$
	$\eta$	(2.6) with (2.2)-(2.4);
$x = 0$	$C$	$\epsilon D_{eff} \nabla C = 0$
	$i_2$	$i_2 = 0$

difference diminishes, which corresponds to the drop in absolute value

of the current. The fact that these two peaks aren't identical testifies to that the charge /discharge processes are not completely reversible.

Figure 5 show the profile of dimensional concentration  $y$  vs. dimensional radial distance  $R$  at 1.6V of the applied potential corresponding to the discharge.

#### 4. Discharge curves.

The battery is discharged from its initial state with  $U_{ini} = 1.9387V$  to 0.01V cutoff voltage at current densities 120.46A/m<sup>2</sup> and 12.05A/m<sup>2</sup>.

The discharge curves of our battery are characterized by plateaus typical to the two-phase system, as Figures 6-7 indicate. The plateau on the open-circuit potential curve and on the discharge curves corresponds to the formation of a new phase, when the potential remains constant. The graph of a larger discharge current lies below that of a smaller one and below the open-circuit potential curve due, firstly, to the contribution of a kinetic term to the expression of a total voltage of the cell. Secondly, the graph of high discharge current takes on zero value earlier, because at larger discharge currents the change of concentration caused by diffusion process, which is associated with the establishment of equilibrium inside the particle, doesn't manage to overtake the change of concentration due to the influx of lithium ions through the surface of the particle, which in this case is large. Thus the given difference between local surface overpotential and the open-circuit potential is attained at smaller average concentrations, i. e. smaller utilizations. That is why the discharge curves, as Figure 10 shows, look contracted in horizontal direction, as compared to the open-circuit potential curve, and the more, the larger is the discharge current.

#### 5. Temperature of the cell.

To determine the temperature of the cell we make the assumptions that the distribution of temperature throughout the cell is uniform at a given instant in time and the enthalpy of mixing and phase-change terms are neglected. With these assumptions the temperature is calculated according to the equation

$$\rho C_p \frac{\partial T}{\partial t} = a_1 h (T_{amb} - T) + i_{app} \left( U - V_{total} - T \frac{d\bar{U}}{dT} \right),$$

where  $\rho$  is the density of the cell,  $C_p$  is the heat capacity the cell, calculated as the average of the components of the cell,  $a_1$  is the ra-

ratio of external cell surface area to geometric electrode surface area,  $a_1 = (2(R_c^2 + RcH))/(R_c^2)$ ,  $T_{amb}$  is the ambient temperature, and  $h$  is the heat transfer coefficient. The entropy term  $\frac{d\bar{U}}{dT}$  is

$$\frac{d\bar{U}}{dT} = \frac{\Re}{F} \ln \left( \frac{1 - y|_{R=1}}{y|_{R=1}} \right).$$

The mean cell heat capacity is calculated by formula:

$$C_p = C_{p,PC} \varrho_{PC} (L_1 \epsilon + L_s \epsilon) + (1 - \epsilon) C_{p,1} \varrho_1 L_1 + C_{p,Li} \varrho_{Li} L_{Li},$$

where  $\varrho_{Li}$ ,  $\varrho_{PC}$ , and  $\varrho_1$  are, respectively, the densities of lithium, propylene carbonate and  $Bi_2Se_3$  electrode;  $C_{p,PC}$ ,  $C_{p,1}$ , and  $C_{p,Li}$  are the heat capacities of propylene carbonate,  $Bi_2Se_3$  electrode, and lithium. Heat parameters of the cell are given in Table III.

**Table III. Heat parameters of the cell.**

Parameter	Value
$T_{amb}$	298 K
$h$	5 W/(m <sup>2</sup> · K)
$\varrho_1$	7500 kg/m <sup>3</sup>
$\varrho_{Li}$	534 kg/m <sup>3</sup>
$\varrho_{PC}$	1200 kg/m <sup>3</sup>
$C_{p,PC}$	720 J/(kg · K)
$C_{p,1}$	190.2798 J/(kg · K)
$C_{p,Li}$	3.72T + 2423 J/(kg · K)

As Figures 8,9 indicate, at smaller discharge currents the cell runs for a longer period of time, as Table IV shows, generating more ohmic heat and, thus, heats to a higher temperature.

**Table IV. Discharge times.**

Model and discharge rate	Time to discharge
$i_{app} = 12.05 A/m^2$	2906 s
$i_{app} = 120.46 A/m^2$	204 s

## 6. Effect of porosity.

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 11, 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, which corresponds to the smaller overall value of the electrolyte concentration in  $Bi_2Se_3$  powdered 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 corresponds 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 12) that there must exist some optimal value of porosity of electrode giving the maximal performance of the battery. Figure 13 verifies this point.

## 7. Conclusions.

We have made a simulation of the cycling of lithium cell with  $Bi_2Se_3$  powder electrode under potentiodynamic control. The obtained voltammograms correspond to those of the two-phase systems with phase change, characterized by two peaks, the one of which corresponds to the discharge, the other - to the charge of the battery.

We have obtained discharge curves typical to the two-phase system with phase change. We have obtained the graphs of absolute temperature vs. utilization testifying to that at smaller discharge currents the battery heats to higher temperature.

We have made a simulation of the discharge of lithium cell with

$Bi_2Se_3$  powdered electrode under galvanostatic control at different values of the porosity of electrode. Two competing factors play role in the discharge. The one increases with the value of the porosity of electrode, the other decreases. There is an optimal value of the porosity of electrode that gives the maximal performance.

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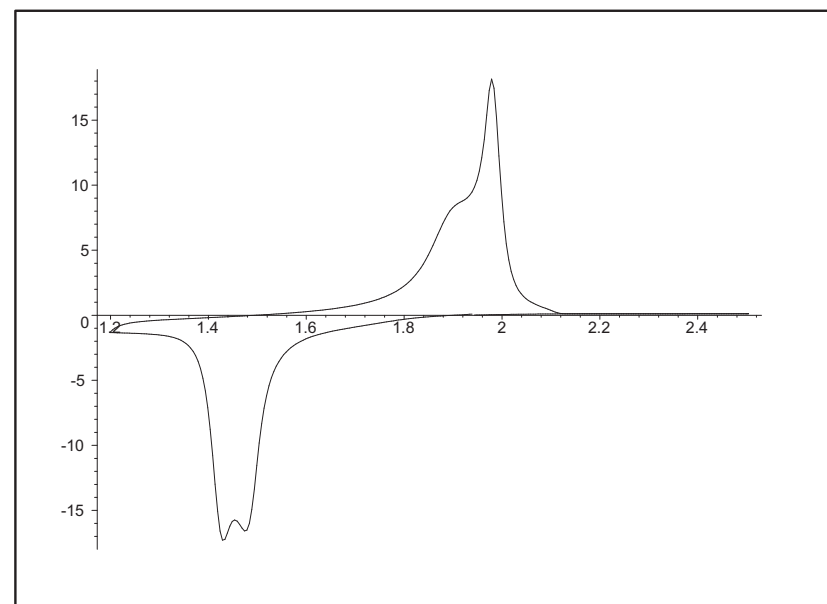


Figure 1. Current density ( $A/m^2$ ) vs. applied voltage ( $V$ ) at scan rate 5mV/s.



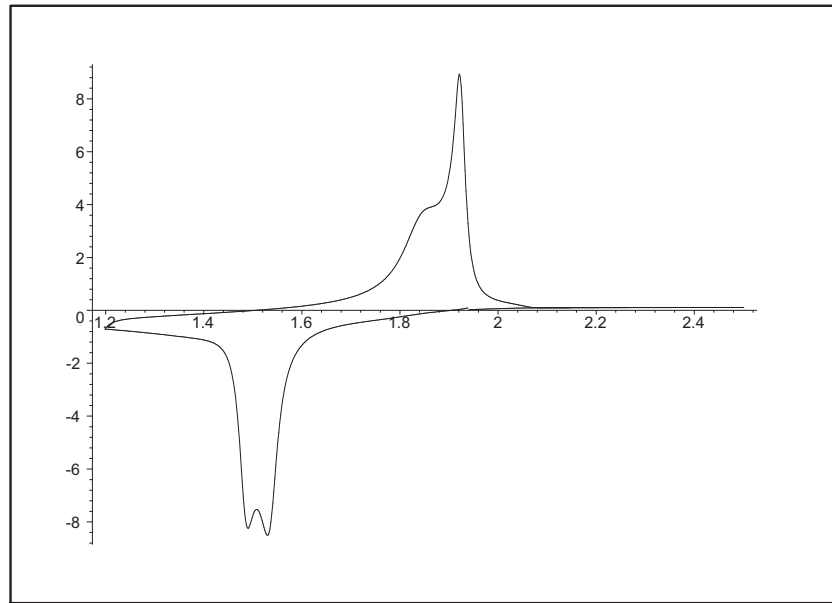


Figure 2. Current density ( $A/m^2$ ) vs. applied voltage ( $V$ ) at scan rate 2mV/s.

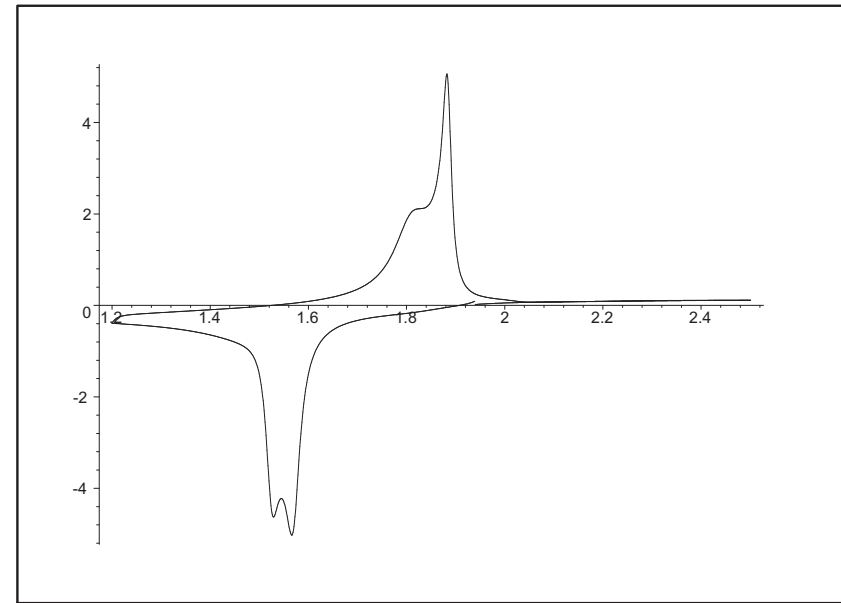


Figure 3. Current density ( $A/m^2$ ) vs. applied voltage ( $V$ ) at scan rate 1mV/s.

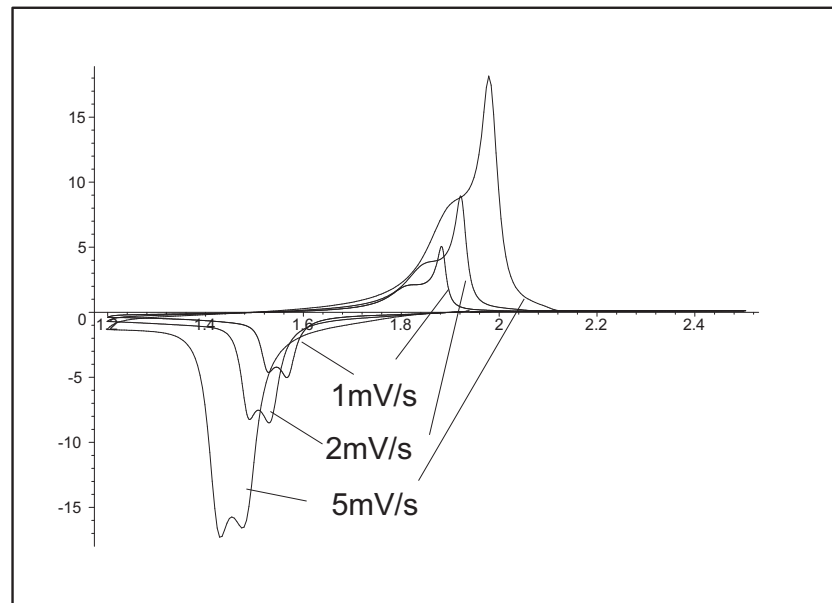


Figure 4. Comparison of graphs of current density ( $A/m^2$ ) vs. applied voltage ( $V$ ) at scan rates 1mV/s, 2mV/s, 5mV/s.

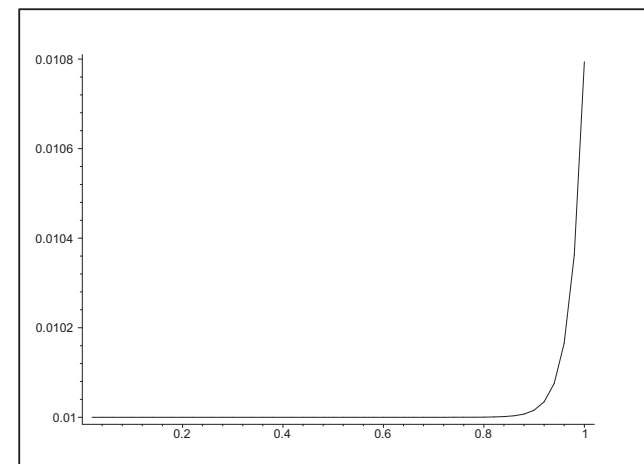


Figure 5. Profile of dimensionless concentration vs. dimensionless radial distance at distance  $L_1/2$  from current collector at applied voltage  $U_{app}=1.6V$ .

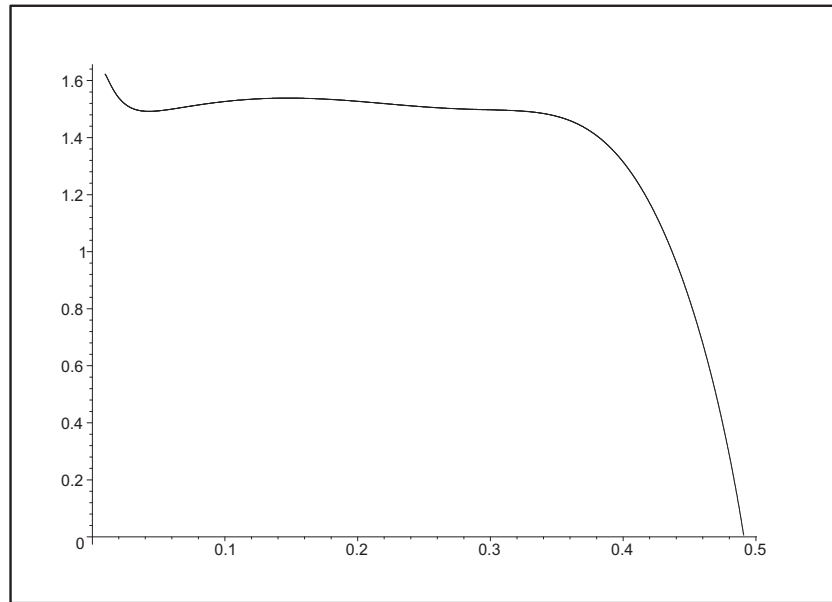


Figure 6. Cell voltage ( $V$ ) vs. utilization at discharge rate  $12.05 \text{ A/m}^2$ .

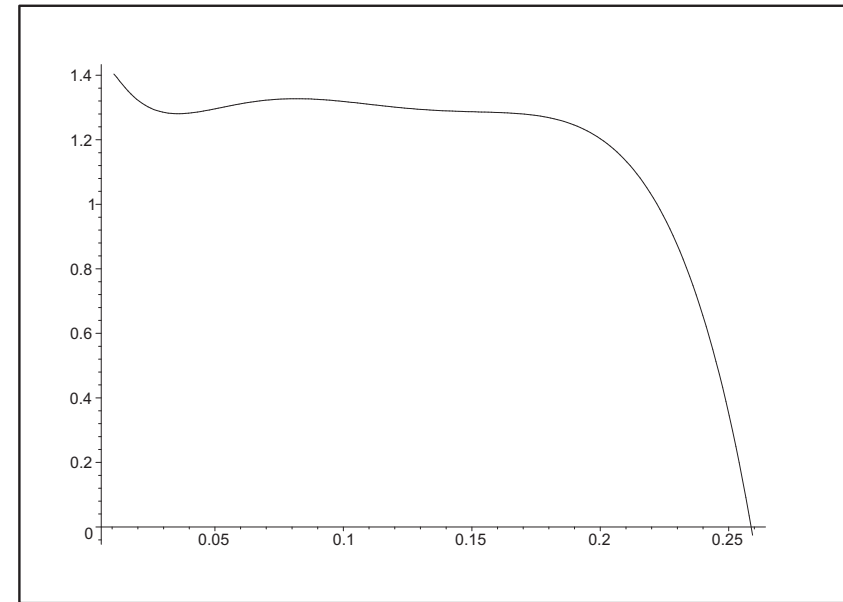


Figure 7. Cell voltage ( $V$ ) vs. utilization at discharge rate  $120.46 \text{ A/m}^2$ .

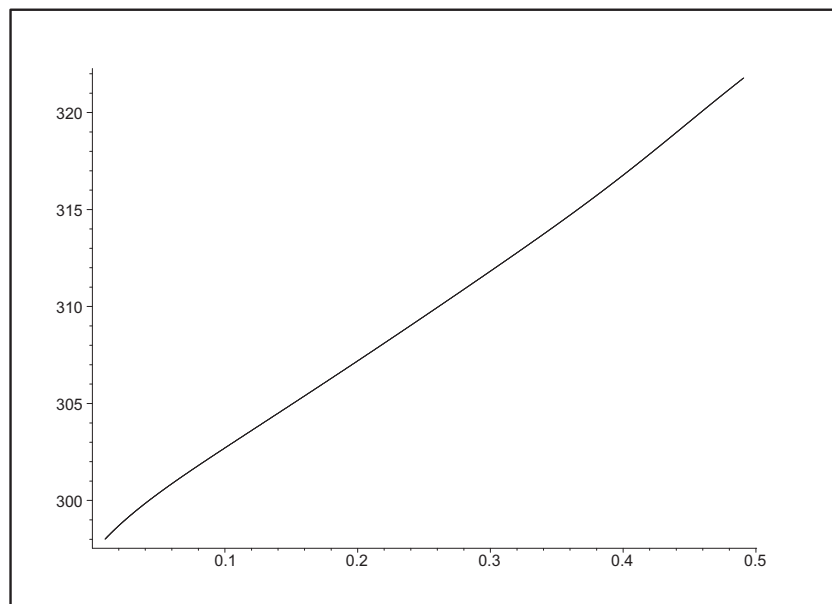


Figure 8. Temperature of the cell ( $K$ ) vs. utilization at discharge rate  $12.05 \text{ A/m}^2$ .

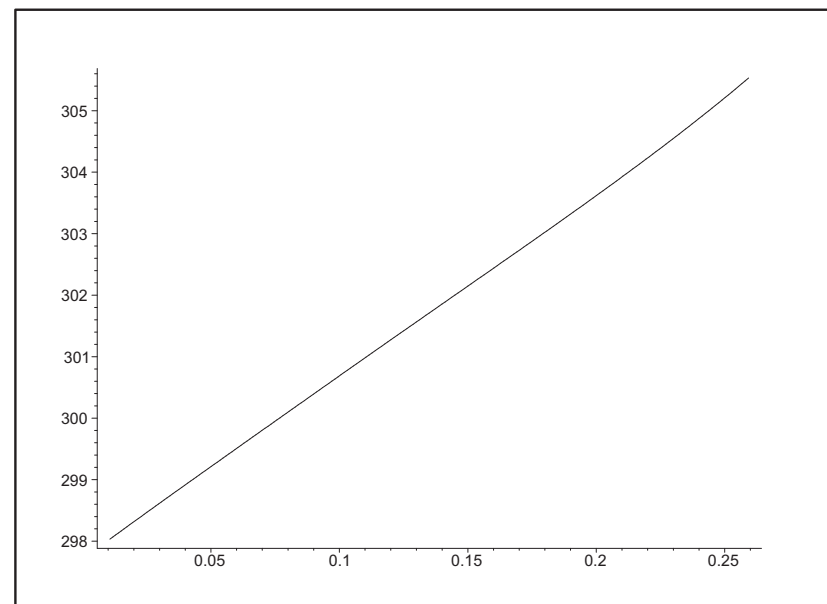


Figure 9. Temperature of the cell ( $K$ ) vs. utilization at discharge rate  $120.46 \text{ A/m}^2$ .

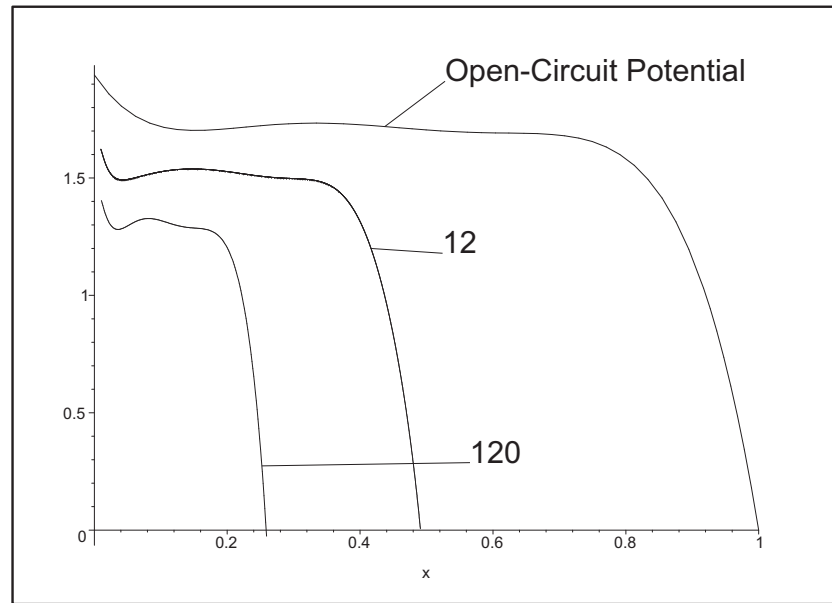


Figure 10. Comparison of cell voltage ( $V$ ) curves at discharge rate,  $12.05 \text{ A/m}^2$  and  $120.46 \text{ A/m}^2$ , and of the open-circuit potential.

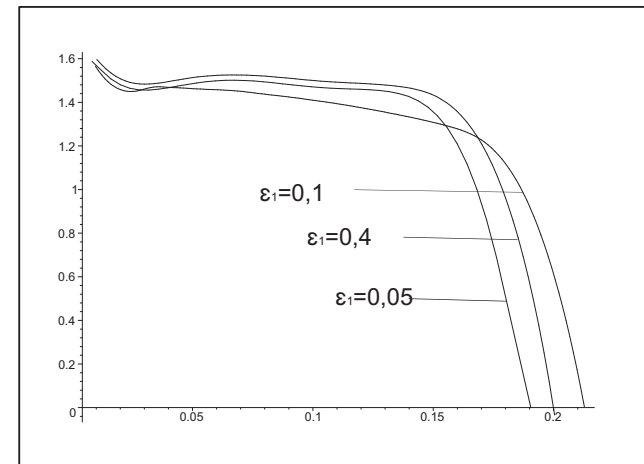


Figure 11. Cell voltage ( $V$ ) vs. utilization at the values of the porosity of electrode  $\epsilon_1 = 0.05$ ,  $\epsilon_1 = 0.1$  and  $\epsilon_1 = 0.4$ , and the porosity of separator  $\epsilon_s = 0.7$ .

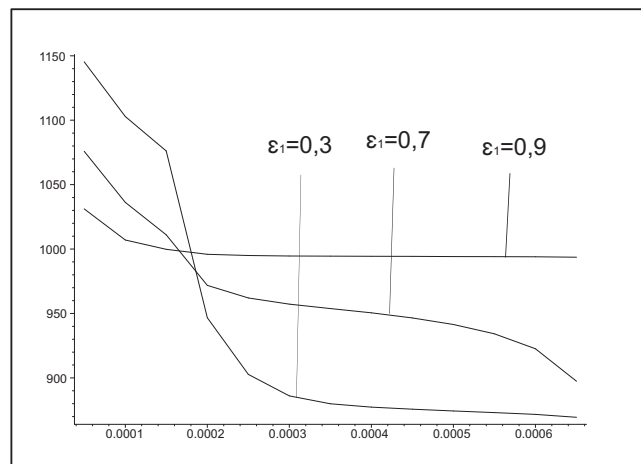


Figure 12. Concentration of the electrolyte vs. distance across the cell at the values of the porosity of electrode  $\varepsilon_1 = 0.3$ ,  $\varepsilon_1 = 0.7$  and  $\varepsilon_1 = 0.9$ , and the porosity of separator  $\varepsilon_s = 0.7$ .

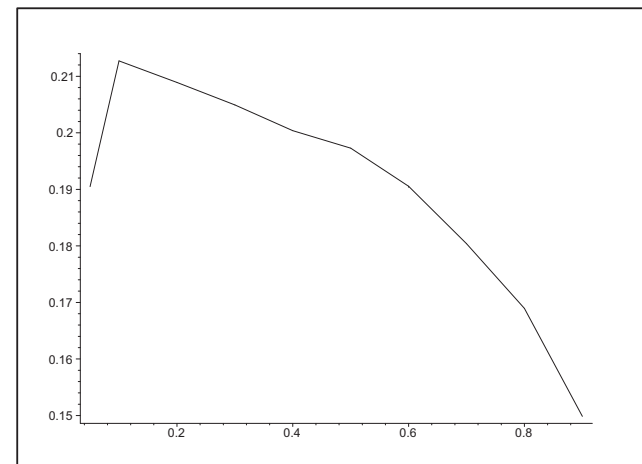


Figure 13. Performance of the cell (utilization at 0.01V) vs. porosity of electrode at the value of the porosity of separator  $\varepsilon_s = 0.7$ .