

On the Diffusion-controlled Transport and Accumulation of Lithium in an Electrode of a Lithium-based Galvanic Cell

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ABSTRACT

The presented formulation in this paper provides the information in the form of lithium concentration profiles and lithium accumulation in the solid-state active material particles of a porous bed cathode of a lithium based galvanic cell as a function of dimensionless time during the cell discharge period under the condition of lithium diffusion in the cathode active material being a predominant process affecting the cell voltage versus time performance. The computed data is deemed to be useful in the predetermination of required cell discharge time corresponding to a desired state-of-charge of a lithium-based galvanic cell under the above-mentioned condition.

KEYWORDS: Diffusion-controlled lithium transport, discharge of a lithium-based galvanic cell

I. INTRODUCTION

The formulation provided in this article is for a lithium-based galvanic cell where the cell discharge behavior is controlled by the very low values of lithium ion or lithium (as $\text{Li}^{+\delta}$ –

$e^{-\delta}$) diffusivity in the microscopic channels (e.g., size range: 1.5 – 5.0 Å) in the active material particles of micrometer radii in a porous bed of a cell cathode as shown in the following sketch for example

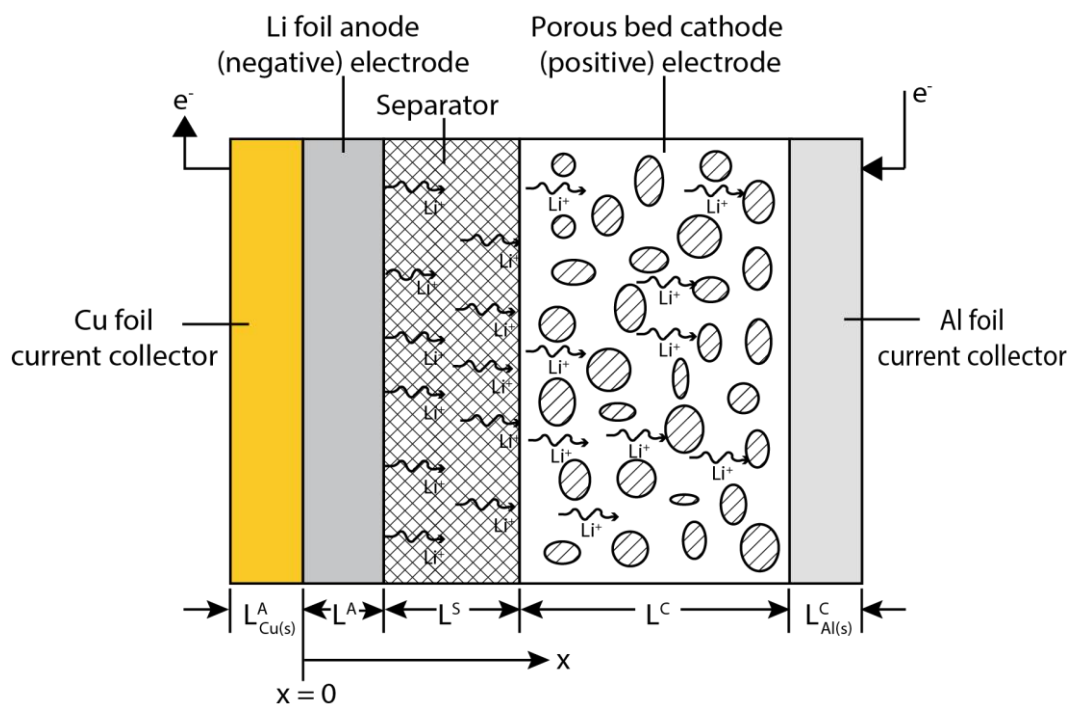


Figure 1. Sketch of a lithium-based galvanic cell during the discharge period.

Notation: L^A , L^S , and L^C = thickness of lithium foil anode electrode, porous separator - containing a lithium electrolyte

solution in its pores, and a porous bed cathode electrode - containing the electrolytic solution in the macro-pores

between the micro-meter active material particles, respectively.

$L_{Cu(s)}^A$, $L_{Al(s)}^C$ = thickness of the anode and cathode electrode current collector, respectively.

In a porous bed cathode, where the solid active material particles (as shown in Figure 1) are wetted by a lithium electrolyte solution present in the macro-pores between them; the discharge behavior of a lithium-based galvanic cell of the type shown in Figure 1 is generally controlled by the lithium movement in the micro-channels, present in the active material, towards the particle centroids. In the discharge of a cell of the type shown in Figure 1, lithium ions are generated at the cell anode-electrolyte solution interface and enter the electrolytic solution in the pores of the separator while the electrochemical reaction generated electrons enter the anode current collector copper (solid) for their supply to an external electrical load circuit. Lithium ions move through the electrolytic solution in the separator and porous bed cathode to arrive at the cathode active material particle-electrolyte solution interfaces. There they interact with the electrons transported by an electronic conductor; for example, graphene or carbon nanotubes (CNT's); from the cathode current collector, Al (s) sheet which receives electrons from the external electrical load circuit. It has been found that the lithium diffusion in the solid active material particles of a lithium-based cell, with their radii of the micrometer size or greater is the slowest process [1]. Therefore, the dynamic (transient) lithium diffusion in the solid-state active cathode active materials is the predominant process in the control of actual cell voltage versus time. Naturally, then; it behooves that a model, based on lithium diffusion in the channels of the cell cathode active material particles, be made available to predict the dynamic discharge current during the cell discharge period. It is here deemed that if a lithium-based cell of the type shown in Figure 1 is discharged at a dynamic cell current level predicted by the model developed based on the lithium diffusion in the channels of the cathode active material particles would result in the minimum loss of the Gibbs free energy change of the overall cell reaction of lithium with an active material of the cell cathode; hence, minimum loss in the actual cell voltage. Also, this means that a very high probability of complete utilization of channels of lithium intercalation type of materials (e.g., $Li_xCoO_2(s)$, $Li_xMn_2O_4(s)$, $Li_xFePO_4(s)$; metal phthalocyanines (MPc) e.g., $Li_xFePc(s)$, $Li_xCuPc(s)$) as well as of the complete utilization of the active material of the conversion type, e.g., $Li_xCF(s)$.

Lithium diffusion in the very narrow channels of lithium intercalation type material, lithium (as $Li^{+\delta} - e^{-\delta}$ form) interacts with the atoms of the active material constituting the

channel walls. Lithium jumps from one site to the next under the thermal (temperature) effect. This type of diffusion may be called configurational type of diffusion coupled with the lithium concentration spatial gradient in the solid-state active material particles. Similarly, lithium diffuses through the channels of a conversion type material such as: $Li_xCF(s)$, for the reaction: $(Li^{+\delta} - e^{-\delta}) + CF(s) \rightarrow LiF(s) + C(s)$. Configurational type mass diffusivity in the solid materials can vary from 10^{-6} to 10^{-14} cm^2sec^{-1} [1 - 4] depending on the channel radius in the active material of a cell electrode. Ending of this introductory section naturally leads us to Section II – Theoretical formulation.

II. THEORETICAL FORMULATION

Transient diffusion of lithium into a spherical active material particle, for example, metal phthalocyanine (MPc), such as iron Pc, copper Pc, etc., in the porous packed bed cathode of a lithium-based cell during its discharge period, with the assumed constant mass diffusivity, is given [5] by

$$\frac{\partial c_s^C}{\partial t} = D \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s^C}{\partial r} \right) \right] \quad (1)$$

where c_s^C = molar concentration of lithium in the cathode active material particles in contact with the electrolytic solution in a galvanic cell, $\left[\frac{mol}{cm^3} \right]$; D = mass diffusivity of lithium in the active material of a galvanic cell electrode, $\left[\frac{cm^2}{s} \right]$; t = time, [sec]; and r = radial distance, [cm].

The solution of the partial differential equation (1), with some adjustment is provided [6] by the following equation:

$$= 1 + \frac{2R_p}{\pi r} \sum_{n=1}^{n=\infty} \left[\frac{(-1)^n}{n} \sin \left(\frac{n\pi r}{R_p} \right) e^{-\left\{ \left(\frac{Dt}{R_p^2} \right) (n\pi)^2 \right\}} \right] \quad (2)$$

where $c_{s,ini}^C$ and $c_{s,0}^C$ are the initial concentration and the concentration at $r = R_p$, respectively, of lithium in the active material of a particle of a porous packed bed electrode.

The total amount of diffusing lithium; which has entered the spherical particle during the cell discharge period, t [sec]; is given by the following derived expression:

$$\left(\frac{N_t^C}{N_\infty^C} \right) = 1 - \left(\frac{6}{\pi^2} \right) \sum_{n=1}^{n=\infty} \left[\frac{1}{n^2} e^{-\left\{ \left(\frac{Dt}{R_p^2} \right) (n\pi)^2 \right\}} \right] \quad (3)$$

where N_t , N_∞ = lithium amount, [moles], accumulated in the cell electrode active material particle in time, t (sec), and $t = \infty$ (sec), respectively.

Solutions corresponding to Eq. (2) and (3), respectively, for short times during the discharge period of lithium-based galvanic cell are given as follows:

$$\left(\frac{c_s^C - c_{s,ini}^C}{c_{s,0}^C - c_{s,ini}^C}\right) = \left[\frac{\left(\frac{c_s^C}{c_{s,0}^C}\right) - \left(\frac{c_{s,ini}^C}{c_{s,0}^C}\right)}{1 - \left(\frac{c_{s,ini}^C}{c_{s,0}^C}\right)}\right] = \left(\frac{R_p}{r}\right) \sum_{n=0}^{\infty} \left[\operatorname{erfc}\left\{\frac{(2n+1)R_p - r}{2\sqrt{Dt}}\right\} - \operatorname{erfc}\left\{\frac{(2n+1)R_p + r}{2\sqrt{Dt}}\right\} \right] \quad (4)$$

$$\left(\frac{N_t^C}{N_{\infty}^C}\right) = 6 \left(\frac{Dt}{R_p^2}\right)^{\frac{1}{2}} \left[\frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} \operatorname{ierfc}\left(\frac{nR_p}{\sqrt{Dt}}\right) \right] - 3 \left(\frac{Dt}{R_p^2}\right) \quad (5)$$

It is here noted that Eq. (2) through (5) can also be expressed in terms of two dimensionless variables, $x = \left(\frac{r}{R_p}\right)$ and $\tau = \left(\frac{Dt}{R_p^2}\right)$. Values of error function ($\operatorname{erf}(\alpha)$), complementary error function ($\operatorname{erfc}(\alpha)$), and integral of the complementary error function ($\operatorname{ierfc}(\alpha)$) are available in [6] for the computational work.

If $L^C =$ thickness of a porous, packed bed cathode of a galvanic cell; $\epsilon^C =$ void fraction, $f_{\text{active}}^C =$ volume fraction of the active material in the solid phase, and $q^C =$ the cathode solid phase active material capacity to store charge; per unit volume of the solid active material, then; corresponding to unit geometric area, the maximum amount of charge which can be stored in the cell cathode is given by:

$$Q_{\text{max}}^C = f_{\text{active}}^C (1 \times L^C) (1 - \epsilon^C) q^C = f_{\text{active}}^C L^C (1 - \epsilon^C) q^C, [\text{Coulombs}] \quad (6)$$

Maximum g-moles of lithium, that can be accumulated in the channels of an active material of narrow size range (e.g., 2 – 3.5 Å), is then given as:

$$N_{\text{max}}^C = \frac{Q_{\text{max}}^C}{F} = \frac{f_{\text{active}}^C L^C (1 - \epsilon^C) q^C}{F}, \left[\frac{\text{moles of lithium}}{\text{cm}^2_{\text{geom}}} \right] \quad (7)$$

Also, if $I \left[\frac{\text{A}}{\text{cm}^2_{\text{geom}}} \right]$ is the geometric current density during the discharge period of a lithium-based cell; then, the lithium amount accumulated in time period, t [sec], is given by:

$$N_t^C = \left(\frac{\int_0^t I dt}{F} \right), \left[\frac{\text{moles of lithium}}{\text{cm}^2_{\text{geom}}} \right] \quad (8)$$

for transient (dynamic) I , and

$$N_t^C = \frac{It}{F}, \left[\frac{\text{moles of lithium stored}}{\text{cm}^2_{\text{geom}}} \right] \quad (9)$$

for constant I . From Eq. (7) and (9), one obtains the following relation:

$$\left(\frac{N_t^C}{N_{\text{max}}^C}\right) = \frac{It}{f_{\text{active}}^C L^C (1 - \epsilon^C) q^C} \quad (10)$$

Assuming the cell discharge geometric current density, I , is at such a low value that the lithium-ion concentration and electric fields are uniform in the electrolytic solution; consequently, the interfacial current density, $\left[\frac{\text{A}}{\text{cm}^2_{\text{surf}}} \right]$, at the interfacial area between the cathode active material particles and electrolytic solution would be the same. For the assumed equal size cathode active material particles, from Eq. (3) and (10) one obtains the following resultant expression.

$$\left(\frac{N_t^C}{N_{\infty}^C}\right) = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left[\frac{e^{-\left\{\left(\frac{Dt}{R_p^2}\right)(n\pi)^2\right\}}}{n^2} \right] = \frac{It}{f_{\text{active}}^C L^C (1 - \epsilon^C) q^C} \quad (11)$$

The result in Eq. (11) leads to:

$$\sum_{n=1}^{\infty} \left[\frac{e^{-\left\{\left(\frac{Dt}{R_p^2}\right)(n\pi)^2\right\}}}{n^2} \right] = \frac{\pi^2}{6} \left[1 - \frac{It}{f_{\text{active}}^C L^C (1 - \epsilon^C) q^C} \right] \quad (12)$$

Note that the geometric current density I has positive sign.

If a lithium-based galvanic cell is discharged at such a low geometric current density, I , so that all the spherical active material solid particles of equal size are uniformly lithium intercalated; then, the lithium mass diffusivity in the channels of the cathode active material as a function of time can be determined from Eq. (12). If D would be observed to change with respect to time, this behavior would be indicative of the change in the resistance to lithium intercalation in the channels of the cathode active material.

Expressing Eq. (11) as:

$$It = (f_{\text{active}}^C L^C (1 - \epsilon^C) q^C) \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{e^{-\left\{\left(\frac{Dt}{R_p^2}\right)(n\pi)^2\right\}}}{n^2} \right] \right) \quad (13)$$

If D is known as a function of the cell discharge time, t [sec], then, Eq. (13) can be employed to predict the quantity, It , as a function of time. The electrolyte solution-cathode active material interfacial current density, $i_s^C \left[\frac{\text{A}}{\text{cm}^2_{\text{surf}}} \right]$, is related to the geometric current density, $I \left[\frac{\text{A}}{\text{cm}^2_{\text{geom}}} \right]$, via the following equation:

$$i_{surf}^C = \frac{I}{a_{surf}^C L^C} \quad (14)$$

For a given cell porous cathode electrode, the electrolyte solution-active material interfacial area per unit porous bed volume, $a_{surf} \left[\frac{cm^2_{surf}}{cm^3_{bed}} \right]$, is given by:

$$a_{surf} = \frac{m_{active}^C S_g^C}{L^C A_{x-area}^C} \quad (15)$$

where m_{active}^C = mass of active material particles [gm] in the cell porous bed cathode, S_g^C = solid particle surface area per gram of the active material, $\left[\frac{cm^2_{surf}}{gm} \right]$, A_{x-area}^C = porous cathode bed cross-sectional area $[cm^2_{geom}]$, [perpendicular to the x coordinate shown in Figure 1]. For the lower value of I controlled by lithium diffusivity, D; consequently, resulting in low i_{surf}^C values; the Butler-Volmer equation [3] simplifies to:

$$i_{surf}^C = i_0^C \left[\frac{(\alpha_a^C + \alpha_c^C)F}{RT} \right] \eta_s^C \quad (16)$$

where i_0^C = exchange current density, $\left[\frac{A}{cm^2_{surf}} \right]$, at the electrolyte solution-cathode active material interface temperature, T [K];

α_a^C, α_c^C = charge transfer coefficients in the electrochemical reaction in the anodic and cathodic direction, respectively.

F = Faraday's constant = $96487 \frac{Coulomb}{g-equivalent}$

R = universal gas constant = $8.3143 \frac{J}{mol \cdot K}$ and

η = surface overpotential, [V], = $(E^C - U^C) = [(actual\ electrode\ potential) - (equilibrium\ electrode\ potential)]$, [V];

noting that when $E^C = U^C$; $i_{surf}^C = 0 \left[\frac{A}{cm^2_{surf}} \right]$ because net reaction rate becomes equal to zero.

For the intercalation type of active material in a cell cathode, i_0^C depends on the electrolytic solution adjacent to the cathode active material particle surface, temperature, and the nature of the active material surface, i.e., free active sites for chemisorption of lithium as well as lithium concentration in the solid active material particle; especially, on the solid side of the interface between the solid active material particle and the electrolytic solution.

If the values of the kinetics parameters of i_0^C, α_a^C , and α_c^C are known; the cell electrochemical reaction polarization voltage loss at the cathode – electrolytic solution interface, η_s^C , for a geometric current density, I, can be determined using Eq. (14) and (16). Then, η_s^C value can be used to determine the actual cell voltage for a geometric current density controlled by the lithium diffusion in a cell cathode-active material of the lithium intercalation type, for example, iron phthalocyanine, copper phthalocyanine, etc. If the values of the parameters i_0^C ,

α_a^C , and α_c^C are not known, one can determine the value of the lumped parameter $[i_0^C(\alpha_a^C + \alpha_c^C)]$ at a temperature T value corresponding to i_{surf}^C value given by Eq. (14) and (13) at one time, t value and experimentally obtaining the value of $\eta_s^C = (E^C - U^C)$, [V], at that i_{surf}^C corresponding to I dictated by Eq. (13). Then, the lumped parameter $[i_0^C(\alpha_a^C + \alpha_c^C)]$ can be used to predict η_s^C at the same T value, for different values of the geometric current density I corresponding to different t values during the discharge of a cell whose cell current is controlled by the lithium diffusion in the channels of the cell cathode active material.

The above provided formulation suggests that if the lithium diffusion in the cell cathode active material controls the cell voltage versus time behavior during the cell discharge period; then, performing the cell discharge at I values as a function of time predicted by Eq. (13), is very likely to result in the complete or near-complete utilization of the cathode active material capacity for lithium or charge storage.

III. DISCUSSION OF THE ANALYTICAL CALCULATED DATA

Figures 2 and 3 present the calculated data from Eq. 2 and 5, respectively. In Figure 2, it is apparent that the lithium penetration, controlled by diffusion, towards the center of an active material particle of a porous bed cathode electrode increases as the cell discharge time, expressed in the dimensionless form τ , increases. For example, the lithium penetration corresponds to approximately the dimensionless radial distance of $x = 0.7$ and 0.1 , respectively, in the dimensionless cell discharge time of $\tau = 0.005$ and 0.03 . For a typical diffusivity value of $10^{-12} \left[\frac{cm^2}{s} \right]$ and the cathode active material particle radius of $1 \mu m$, these τ values correspond to 50 and 300 seconds, respectively. This implies that the particle active material channels within $x = 0.7$ and 0.1 remain unutilized corresponding to these cell discharge times. At $\tau = 0.05$ (equivalent to 500 seconds), the lithium penetration to the particle center, $x = 0$, as well as its accumulation (equivalent to charge accumulation) is shown there. As τ increases, the dimensionless lithium concentration profile moves “up” towards its value of 1.0 almost everywhere inside the channels of a spherical particle of a cell cathode active material (e.g., $V_2O_5(s)$, $CuPc(s)$, etc.). The concentration profile at $\tau = 0.35$ corresponding to the actual cell discharge time of 3,500 sec (= 0.9722hr) or 350,000 sec (= 97.22hr) for a cathode active material possessing lithium diffusivity of 10^{-12} or $10^{-14} \left[\frac{cm^2}{s} \right]$, in the active material particle of radius equal one micrometer. This result is significant in that the cell discharge time required to utilize the active material to any extent (i.e., degree) is highly dependent on the lithium diffusivity in the active material of

a given cell cathode at its temperature during the cell discharge period.

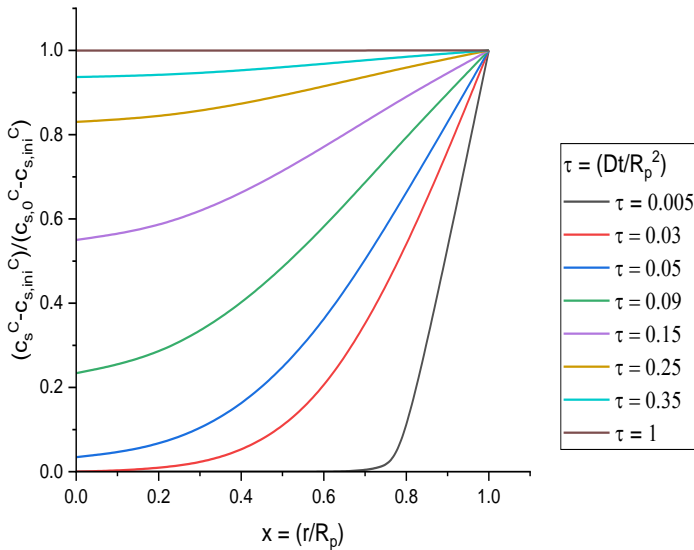


Figure 2. Dimensionless lithium concentration distribution profiles in a spherical, active material solid particle of a porous bed electrode of a lithium-based galvanic cell; with the initial lithium concentration = $c_{s,ini}^C$ and the surface lithium concentration = $c_{s,0}^C$.

Figure 3 shows the fractional accumulation of lithium in an active material spherical particle of a porous bed cathode electrode during the discharge period of a lithium-based cell. At the start of a lithium-based cell discharge, the fractional accumulation of lithium represented by $\left(\frac{N_f^C}{N_\infty^C}\right)$ appears to be of exponential type. The rate of change of $\left(\frac{N_f^C}{N_\infty^C}\right)$ with respect to τ decreases as the lithium accumulation in the cathode active material particle approaches towards the saturation of the solid cathode active material with lithium. At $\tau = 0.4$, $\left(\frac{N_f^C}{N_\infty^C}\right) \cong 1.0$, suggestive of almost complete utilization of the capacity of a cathode active material for lithium or charge storage. It is here noted that $\tau = 0.4$ is equivalent to actual cell discharge time of 4,000.0 sec (= 1.111hr) and 400,000.0 sec (= 111.111hr) corresponding to $D = 10^{-12}$ and $10^{-14} \left[\frac{\text{cm}^2}{\text{s}}\right]$, respectively.

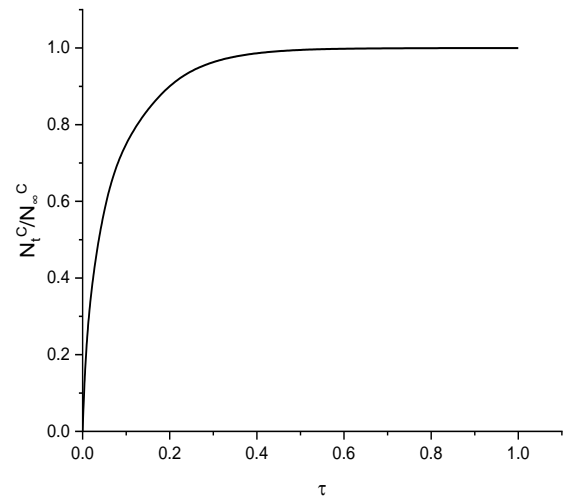


Figure 3. Fractional accumulation of lithium in an active material spherical solid particle of a porous bed cathode of a lithium-based galvanic cell during its discharge period.

Figure 4 shows the dimensionless lithium concentration profiles for short discharge period of a lithium-based galvanic cell as computed from Eq. (4). These profiles are similar to those shown in Figure 2. Here, the dimensionless time of $\tau = 0.02$ is equivalent to the actual discharge time of $t = 200.0$ and $20,000.0$ sec, respectively, corresponding to the lithium diffusivity of 10^{-12} and $10^{-14} \left[\frac{\text{cm}^2}{\text{s}}\right]$ in a cathode active material particle of $1 \mu\text{m}$ radius. Figure 5 shows the accumulation of lithium or charge in the solid active material particles of a porous bed cathode electrode during short discharge period of a lithium-based cell. At $\tau = 0.01$, the fractional accumulation of lithium or charge equal to 0.30 is observed. This $\tau = 0.01$ is equivalent to the actual discharge time, $t = 100.0$ and $10,000.0$ [sec], corresponding to the lithium diffusivity of 10^{-12} and $10^{-14} \left[\frac{\text{cm}^2}{\text{s}}\right]$ in a particle of micrometer radius of a porous bed cathode electrode of a lithium-based cell.

The electrochemical reaction polarization voltage loss, η_s^C , associated with the net cathodic direction reaction can be determined from Eq. (16) using the predicted geometric current density, I , from Eq. (13) at any time during the cell discharge period. However, the requirement is that the values of the electrode reaction kinetics parameters; i_0^C , α_a^C , α_c^C be made available. Also, the solid particle surface area per unit mass of the cathode active material, S_g^C , determined through experimental measurements, should be made available to calculate the electrolyte solution–cathode active material interfacial current density, i_s^C , for its use in Eq. (16) to calculate η_s^C . This voltage loss, in combination with other

voltage losses associated with the electrochemical reaction polarization at the cell anode and ionic transport through solid films and electrolytic solution, can be used to predict the cell voltage at any time during the discharge period of a lithium-based cell or battery. This is done by subtracting the sum of the voltage drops, associated with the individual processes occurring in a cell delivering electric power, from the cell emf (open-circuit electric potential difference) corresponding to the cell state-of-charge (SOC) at that time.

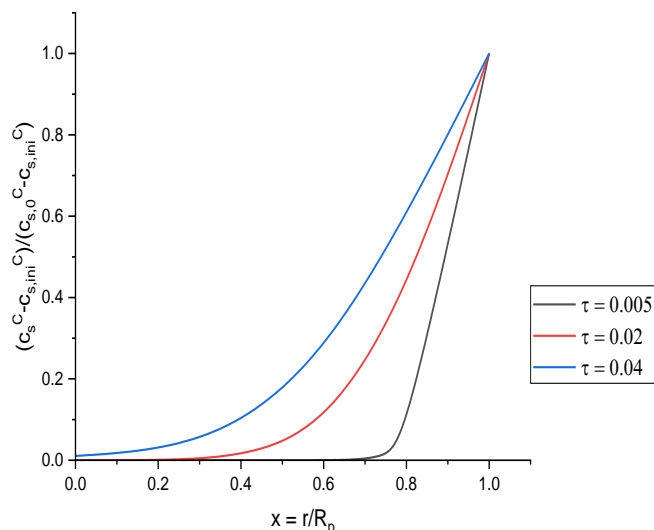


Figure 4. Typical dimensionless lithium concentration distribution in a spherical, active material solid particle of a porous bed cathode electrode of a lithium-based galvanic cell during its short discharge period.

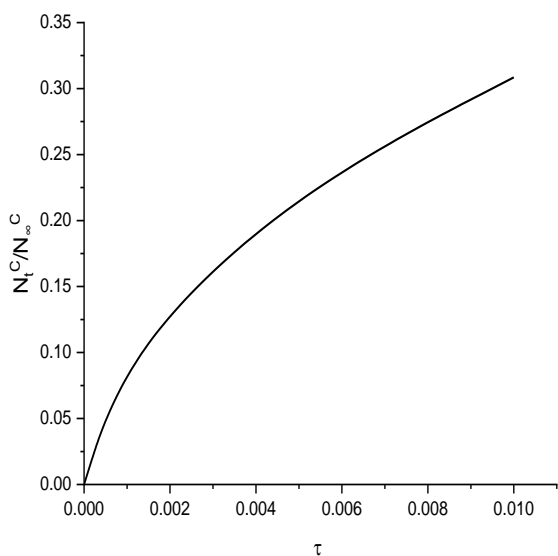


Figure 5. Accumulation of lithium in an active material spherical solid particle of a porous bed cathode of a lithium-based galvanic cell during its short discharge period.

IV. CONCLUDING REMARKS

- Theoretically developed formulation provides insight into the lithium transport and accumulation in a spherical particle of a lithium-intercalation type active material of a porous bed cathode of a lithium-based galvanic cell under the condition of lithium diffusion in the cathode active material being the predominant process affecting the cell discharge behavior (i.e., actual cell voltage versus time).
- The theoretical predicted data presented in the form of plots is deemed to be very helpful in obtaining the required cell discharge time for complete or near-complete utilization of the charge-storage capacity of a cathode active material depending on the lithium diffusivity in a solid spherical particle at the cell cathode operational temperature.
- Although the focus of this presentation is on the lithium diffusion in the solid-state particles of a lithium-intercalation type active material of a porous bed cathode of a lithium-based galvanic cell as the predominant process affecting the cell discharge behavior; however, application of this formulation can be extended, with some adjustments, to assess the effect of lithium diffusion in the active material particles of a porous bed anode (negative) electrode of a lithium-based galvanic cell on its performance behavior during its discharge period.

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