Shrinking Core Model Formulation for the Electrochemical Performance Analysis of a Lithium/Carbon Monofluoride Cell

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ARTICLE INFO	ABSTRACT
Published Online: 21 March 2023	A shrinking core model formulation has been developed based on lithium-ion diffusion through the product layer of carbon monofluoride cathode active material being the predominate mechanism controlling the cell discharge behavior. The formulation expresses the cell discharge time; speed of the moving reaction zone towards the center of a spherical active material, carbon monofluoride, particle; cell current, and the fractional amount of charge involved in the cell electrochemical reaction in terms of the fractional conversion of the cell cathode limiting reactant, carbon monofluoride. An experimental data-based correlation between the required, lithium-ion effective diffusivity and cell voltage loss is also provided to explain the cell discharge behavior under the constant current condition.
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KEYWORDS: shrinking core model, carbon monofluoride, lithium, primary, diffusion-limited	

I. INTRODUCTION

The work reported in this paper is related our recent effort to further the development of the lithium-based galvanic cells with the aim of increasing their electric power and energy densities [1, 2]. A typical, lithium/electrolyte/ CF(s), cell is sketched in Figure 1 [2].

Figure 2 shows the sketch of an active material, CF$_{(s)}$, particle in the packed bed of the cathode of a cell shown in Figure 1. The active material, CF$_{(s)}$, particle is in contact with an electrolytic solution. Shown in the sketch in Figure 2 are: spatial region I of radius, r_c, contains the yet unreacted solid reactant, CF$_{(s)}$ and the spatial region II ($r_c \leq r \leq R$) contains the solid product layer composed of LiF$_{(s)}$ and C$_{(s)}$ resulting from the reaction: CF$_{(s)}$ + Li$_{(s)}$ $\rightarrow$ LiF$_{(s)}$ + C$_{(s)}$. The formulation presented in Section 2 is based on the concept of 'shrinking core' [3].
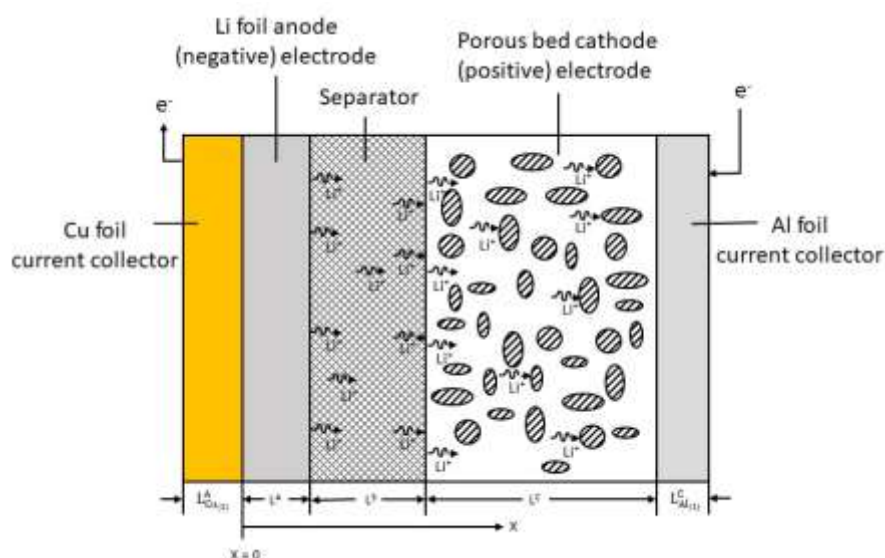

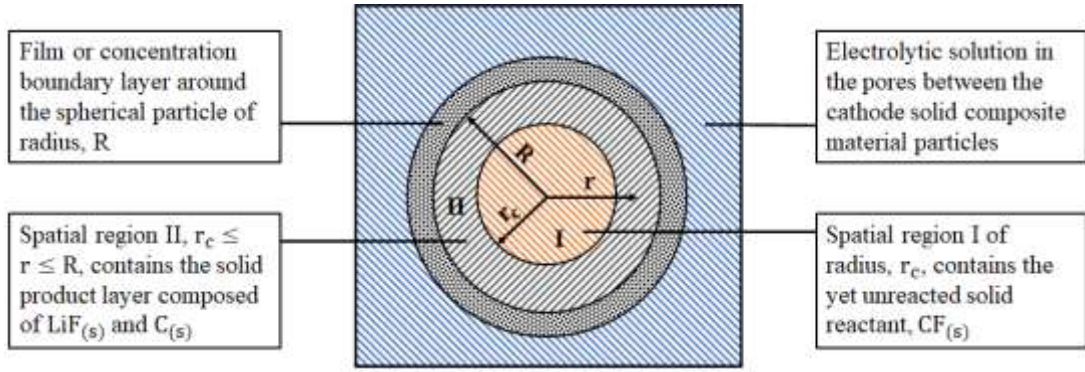**Figure 1:** Sketch [2] of a lithium – based galvanic cell during its discharge period.
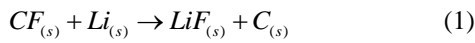
Figure 2: An active material, $CF_{(s)}$, particle in contact with an electrolytic solution during the discharge period of a [lithium/ electrolyte/$CF_{(s)}$] cell.

II. SHRINKING CORE MODEL FORMULATION

It is here assumed that the overall reaction:

$$CF_{(s)} + Li_{(s)} \rightarrow LiF_{(s)} + C_{(s)} \qquad (1)$$

takes place at the surface of the unreacted $CF_{(s)}$ shrinking core. Transport of lithium ions occurs, via diffusion, from the bulk electrolytic solution through the species (ionic and non-ionic) concentration boundary layer and the solid product layer composed of $LiF_{(s)}$ and $C_{(s)}$ to the reactive surface located at the radial distance, $r = r_c$, which is decreasing with the cell discharge time increasing. It is assumed that the reaction time for the reaction of a lithium ion/electron pair with the limiting reactant, $CF_{(s)}$, at the $CF_{(s)}$ shrinking core surface is extremely short relative to the time involved for the lithium ion transport from the bulk electrolytic solution through the species concentration boundary layer and the solid product film surrounding the unreacted solid, $CF_{(s)}$, core. The relevant steps of the model formulation are briefly given below.

With the pseudo-steady state approximation under the isothermal condition, the continuity equation [2] for lithium ions in the solid product region is given as follows:

$$\frac{\partial}{\partial r}\left(D'_{e-Li^+}\left(r^2 \frac{\partial C'_{Li^+-s}}{\partial r}\right)\right) = 0 \quad (2)$$

$$\left(\text{valid for}: \ r_c \leq r \leq R\right)$$

The boundary conditions to solve Eq. (2) are:
At $r = r_c$:

$$\begin{pmatrix} \text{molar flux of lithium ions} \\ \text{arriving at the } CF_{(s)} \\ \text{shrinking core surface at } r = r_c \end{pmatrix} = $$

$$\begin{pmatrix} \text{conversion rate of lithium ions} \\ \text{via rapid reaction of lithium ions} \\ \text{with the solid reactant, } CF_{(s)} \end{pmatrix} \qquad (3a)$$

At $r = R$ (at the particle surface):

$$\begin{pmatrix} \text{lithium molar flux away from} \\ \text{the interface between} \\ \text{the electrolyte solution boundary} \\ \text{layer and the solid particle,} \\ \text{located at } r = R, \\ \text{towards the center of the particle} \end{pmatrix} = $$

$$\begin{pmatrix} \text{molar flux of lithium ions} \\ \text{to the interface from} \\ \text{the bulk electrolyte solution,} \\ \text{throught the electrolytic solution} \\ \text{concentration boundary layer} \\ \text{surrounding the particle} \end{pmatrix} \qquad (3b)$$

Expressing the boundary conditions in terms of symbols:
At $r = r_c$

$$D'_{e-Li^+}\left(\frac{\partial C'_{Li^+-s}}{\partial r}\bigg|_{r=r_c}\right) = k_s C_{CF_{(s)},0}\left(c'_{Li^+-s}\big|_{r=r_c}\right) \qquad (4a)$$

The right-hand side of Eq. (4a), representing the intrinsic surface reaction rate, is related to the Butler-Volmer equation [5] as follows:

$$\left[k_s C_{CF(s),0}\left(C'_{Li^+-s}\right)_{r=r_c}\right] F = i = i_0\left[e^{\frac{(1-\beta)F\eta_s}{RT}} - e^{\frac{-\beta F\eta_s}{RT}}\right] \quad (4b)$$

where i_0 = exchange current density, $\left[\text{ampere cm}^{-2}_{surface}\right]$; η_s = surface overpotential = $E - E^0$, $\left[\text{volt}\right]$; E = electrode actual electric potential; E^0 = electrode equilibrium electric potential when the net of the forward and backward reaction rates is zero; i.e. when $i = 0.0$, $\left[\text{ampere cm}^{-2}_{surface}\right]$; F = Faraday's constant = 96487 Coulombs per g-equivalent and T = temperature, $\left[\text{K}\right]$.

At $r = R$,

$$D'_{e-Li^+}\left(\frac{\partial C'_{Li^+-s}}{\partial r}\bigg|_{r=R}\right) = k_L\left(C^b_{Li^+} - \left(C^S_{Li^+-s}\big|_{r=R}\right)\right) \quad (4c)$$

where C'_{Li^+-s} = molar concentration of lithium ions in the solid product layer region, $r_c \leq r \leq R$, $C_{CF_{(s)},0}$ = molar concentration of the limiting reactant, $CF_{(s)}$ in the cell cathode active material, $CF_{(s)}$, particle, D'_{e-Li^+} = effective diffusivity of lithium ions in the reaction product solid layer containing microchannels, k_s = overall intrinsic electrochemical reaction rate coefficient, k_L = mass transfer coefficient for lithium ion mass transfer through the electrolyte solution concentration boundary layer (or film) surrounding the particle for the lithium ions arrival at the particle surface located at $r = R$, $C^b_{Li^+}$ = molar concentration of lithium ions in the bulk electrolyte solution and $C^S_{Li^+-s}$ = molar concentration of lithium ions in the microchannels of the particle at $r = R$.

Assuming constant D'_{e-Li^+}, Eq. (2) was integrated twice to obtain the general solution. Then, the boundary conditions, Eqs. (4a) and (4b) were used to predict $\left(C'_{Li^+-s} / C^b_{Li^+}\right)$ as a function of radial distance, r, in the solid product layer surrounding the unreacted, $CF_{(s)}$, core in the particle. The developed mathematical expression for $\left(C'_{Li^+-s} / C^b_{Li^+}\right)$ is given by

$$\left(\frac{C'_{Li^+-s}}{C^b_{Li^+}}\right) = \frac{\left(1 + \frac{D'_{e-Li^+}}{k_s C_{CF_{(s)},0} r_c}\right)\frac{1}{r_c} - \frac{1}{r}}{\left(1 + \frac{D'_{e-Li^+}}{k_s C_{CF_{(s)},0} r_c}\right)\frac{1}{r_c} - \left(1 - \frac{D'_{e-Li^+}}{k_L R}\right)\frac{1}{R}} \quad (5)$$

From Eq. (5),

$$\left(\frac{\partial C'_{Li^+-s}}{\partial r}\bigg|_{r=r_c}\right) = \frac{\left(C^b_{Li^+} / r_c^2\right)}{\left[\left(1 + \frac{D'_{e-Li^+}}{k_s C_{CF_{(s)},0} r_c}\right)\frac{1}{r_c} - \left(1 - \frac{D'_{e-Li^+}}{k_L R}\right)\frac{1}{R}\right]} \quad (6)$$

Gram-moles of the solid reactant, $CF_{(s)}$, in the unreacted core of radius, r_c, at any time is

$$N_{CF_{(s)},pc} = \frac{4}{3}\pi r_c^3 C_{CF_{(s)},0} \quad (7)$$

Rate of decrease in the g-moles of solid, $CF_{(s)}$, in the shrinking core is given by

$$\left(\frac{-dN_{CF_{(s)},pc}}{dt}\right) = -\frac{d}{dt}\left(\frac{4\pi}{3}r_c^3 C_{CF_{(s)},0}\right) \quad (8a)$$

$$= -\left(\frac{4\pi}{3}C_{CF_{(s)},0}\right)\frac{d}{dt}\left(r_c^3\right) = \left(-4\pi r_c^2 C_{CF_{(s)},0}\right)\left(\frac{dr_c}{dt}\right) \quad (8b)$$

Conversion rate of $CF_{(s)}$ by its reaction with (Li^+ ion, e^-) pairs at the reaction front at $r = r_c$ is equal to $\left(\frac{-dN_{CF_{(s)},pc}}{dt}\right)$.

The consumption rate of lithium-ions at the $CF_{(s)}$ shrinking core reaction-front is given by

$$\begin{pmatrix}\text{lithium ions conversion} \\ \text{rate at } r = r_c\end{pmatrix} = \begin{pmatrix}\text{conversion rate of} \\ CF_{(s)}, pc\end{pmatrix}$$

$$= \left(\frac{1 \text{ mole of } Li^+ \text{ ions consumed}}{1 \text{ mole of } CF_{(s)} \text{ consumed}}\right)\left(\frac{-dN_{CF_{(s)},pc}}{dt}\right)$$

$$= \left(4\pi r_c^2 C_{CF_{(s)},0}\right)\left(-\frac{dr_c}{dt}\right) \quad (9)$$

$$\begin{pmatrix}\text{lithium ion consump-} \\ \text{tion rate at } r = r_c\end{pmatrix} = \begin{pmatrix}\text{lithium-ion} \\ \text{arrival rate at } r = r_c\end{pmatrix} \quad (10)$$

$$4\pi r_c^2 C_{CF_{(s)},0}\left(-\frac{dr_c}{dt}\right) = 4\pi r_c^2\left[D'_{e-Li^+}\left(\frac{\partial C'_{Li^+-s}}{\partial r}\bigg|_{r=r_c}\right)\right] \quad (11)$$

Equation (11) leads to:

$$C_{CF_{(s)},0}\left(-\frac{dr_c}{dt}\right) = D'_{e-Li^+}\left(\frac{\partial C'_{Li^+-s}}{\partial r}\bigg|_{r=r_c}\right) \quad (12)$$

Inserting $\left(\left.\dfrac{\partial C'_{Li^+-s}}{\partial r}\right|_{r=r_c}\right)$ from Eq. (6) into Eq. (12) and simplifying,

$$C_{CF_{(s)},0}\left(-\frac{dr_c}{dt}\right)=\frac{D'_{e-Li^+}C^b_{Li^+}}{\left[\left(1+\dfrac{D'_{e-Li^+}}{k_sC_{CF_{(s)},0}r_c}\right)r_c-\left(1-\dfrac{D'_{e-Li^+}}{k_LR}\right)\dfrac{r_c^2}{R}\right]} \qquad (13)$$

Equation (13) is integrated from $'t'=0$ to $'t'=t$ and correspondingly from $'r_c'=R$ to $'r_c'=r_c$ to obtain, after simplification, the following mathematical expression for the time, t, for the arrival of lithium ions at $r=r_c$, is given as:

$$t=\left(\frac{RC_{CF_{(s)},0}}{C^b_{Li^+}}\right)\left[\begin{array}{l}\dfrac{1}{3}\left(\dfrac{1}{k_L}-\dfrac{R}{D'_{e-Li^+}}\right)\left\{1-\left(\dfrac{r_c}{R}\right)^3\right\}\\[4mm]+\dfrac{R}{2D'_{e-Li^+}}\left\{1-\left(\dfrac{r_c}{R}\right)^2\right\}\\[4mm]+\dfrac{1}{k_sC_{CF_{(s)},0}}\left(1-\dfrac{r_c}{R}\right)\end{array}\right] \qquad (14)$$

Re-expressing Eq. (14):

$$t=\left(\frac{RC_{CF_{(s)},0}}{C^b_{Li^+}}\right)\left[\begin{array}{l}\dfrac{1}{3k_L}\left\{1-\left(\dfrac{r_c}{R}\right)^3\right\}\\[4mm]+\dfrac{1}{\left(\dfrac{6D'_{e-Li^+}}{R}\right)}\left\{\begin{array}{l}3\left(1-\left(\dfrac{r_c}{R}\right)^2\right)-\\[3mm]2\left(1-\left(\dfrac{r_c}{R}\right)^3\right)\end{array}\right\}\\[4mm]+\dfrac{1}{k_sC_{CF_{(s)},0}}\left(1-\dfrac{r_c}{R}\right)\end{array}\right] \qquad (15)$$

During the cell discharge period, fractional conversion of the limiting solid reactant, $CF_{(s)}$, at any time when the reaction front is at $r=r_c$, is given by

$$x=\frac{\dfrac{4}{3}\pi R^3C_{CF_{(s)},0}-\dfrac{4}{3}\pi r_c^3C_{CF_{(s)},0}}{\dfrac{4}{3}\pi R^3C_{CF_{(s)},0}}=1-\left(\frac{r_c}{R}\right)^3 \qquad (16)$$

or,

$$\left(\frac{r_c}{R}\right)=\left(1-x\right)^{1/3} \qquad (17)$$

Inserting $\left(\dfrac{r_c}{R}\right)$ from Eq. (17) into Eq. (15) leads to:

$$t=\left(\frac{RC_{CF_{(s)},0}}{C^b_{Li^+}}\right)\left[\begin{array}{l}\dfrac{x}{3k_L}+\dfrac{1}{\left(\dfrac{6D'_{e-Li^+}}{R}\right)}\left\{\begin{array}{l}3\left(1-\left(1-x\right)^{2/3}\right)\\[3mm]-2x\end{array}\right\}\\[4mm]+\dfrac{1}{k_sC_{CF_{(s)},0}}\left(1-\left(1-x\right)^{1/3}\right)\end{array}\right] \qquad (18)$$

Under the condition, $\left(\dfrac{6D'_{e-Li^+}}{R}\right)\Box\left(3k_L\right)$ as well as $\Box\left(k_sC_{CF_{(s)},0}\right)$, Eq. (18) simplifies to:

$$t=\left(\frac{R^2C_{CF_{(s)},0}}{6C^b_{Li^+}D'_{e-Li^+}}\right)\left[3\left\{1-\left(1-x\right)^{2/3}\right\}-2x\right] \qquad (19)$$

For the complete conversion of $CF_{(s)}$ in the active material $CF_{(s)}$ particle, i.e., for $x=1$, Eqs. (18) and (19) are simplified to:

$$t^*=\left(\frac{RC_{CF_{(s)},0}}{C^b_{Li^+}}\right)\left[\frac{1}{3k_L}+\frac{1}{\left(\dfrac{6D'_{e-Li^+}}{R}\right)}+\frac{1}{k_sC_{CF_{(s)},0}}\right] \qquad (20)$$

and

$$t^*=\left(\frac{R^2C_{CF_{(s)},0}}{6C^b_{Li^+}D'_{e-Li^+}}\right) \qquad (21)$$

The reaction speed, to consume $CF_{(s)}$, towards the spherical particle center is obtained using Eq. (13)

$$\dot{r}_c=\left(\frac{-dr_c}{dt}\right)=\left(\frac{D'_{e-Li^+}C^b_{Li^+}}{C_{CF_{(s)},0}r_c}\right)\left[\frac{1}{\left(1+\dfrac{D'_{e-Li^+}}{k_sC_{CF_{(s)},0}r_c}\right)-\left(1-\dfrac{D'_{e-Li^+}}{k_LR}\right)\left(\dfrac{r_c}{R}\right)}\right] \qquad (22)$$

$$\left(\text{valid: } 0\le\frac{r_c}{R}\le1\right)$$

By the use of Eq. (17), Eq. (22) is transformed into the following expression involving the fractional conversion of $CF_{(s)}$, x.

$$\dot{r}_c = \left(\frac{D'_{e-Li^+}C^b_{Li^+}}{RC_{CF_{(s)},0}(1-x)^{1/3}}\right)\left[\frac{1}{\left(1+\dfrac{D'_{e-Li^+}}{k_sC_{CF_{(s)},0}R(1-x)^{1/3}}\right)}-\left(1-\dfrac{D'_{e-Li^+}}{k_LR}\right)(1-x)^{1/3}\right]$$ (23)

$$(\text{valid}: 1 \geq x \geq 0)$$

Under the condition of: $D'_{e-Li^+} \gg \left(k_sC_{CF_{(s)},0}R\right)$ as well as $D'_{e-Li^+} \gg \left(k_LR\right)$; Eq. (23) reduces to:

$$\dot{r}_c = \left(\frac{D'_{e-Li^+}C^b_{Li^+}}{RC_{CF_{(s)},0}}\right)\left[\frac{1}{(1-x)^{1/3}-(1-x)^{2/3}}\right]$$ (23a)

Re-expressing Eq. (23a):

$$S_d = \frac{\dot{r}_cRC_{CF_{(s)},0}}{D'_{e-Li^+}C^b_{Li^+}} = \left[\frac{1}{(1-x)^{1/3}-(1-x)^{2/3}}\right]$$ (23b)

$$(\text{valid}: 1 \geq x > 0)$$

This is the speed of the reaction zone towards the center of the active material, $CF_{(s)}$, particle in the dimensionless form.

The charge involved, according to Eq. (1), for $CF_{(s)}$ conversion in the cell cathode active material particle at the time, when the shrinking core reaction front is at $r = r_c$, is given by:

$$Q_{\text{part, charge involved}} = \left(\frac{4}{3}\pi R^3C_{CF_{(s)},0}F\right)\left[1-\left(\frac{r_c}{R}\right)^3\right]$$

$$= \frac{4}{3}\pi R^3C_{CF_{(s)},0}Fx$$ (24)

The amount of charge involved for $CF_{(s)}$ conversion completely in an active material particle of the cell cathode during the cell discharge period is given by

$$Q^*_{\text{part, charge involved}} = \frac{4}{3}\pi R^3C_{CF_{(s)},0}F$$ (25)

Dividing Eq. (24) by (25) leads to:

$$\left(\frac{Q_{\text{part, charge involved}}}{Q^*_{\text{part, charge involved}}}\right) = x = \left(1-f_{\text{soc, part}}\right)$$ (26)

where $f_{\text{soc, part}}$ is defined as the charge-fractional capacity of a particle, containing $CF_{(s)}$ active material, still available to accept charge for its reaction with lithium during the cell discharge period. From Eq. (26),

$$f_{\text{soc, part}} = 1-x$$ (27)

Molar conversion rate of the active material, $CF_{(s)}$, in an active material particle of the cell cathode at any time during the cell discharge period is given as:

$$\left(-\frac{dN_{CF_{(s)}}}{dt}\right)_{\text{part}} = \left(4\pi r_c^2\right)\dot{r}_cC_{CF_{(s)},0}$$ (28)

Inserting for $\dot{r}_c$ from Eq. (22) into Eq. (28),

$$\left(-\frac{dN_{CF_{(s)}}}{dt}\right)_{\text{part}}$$

$$= \left(4\pi r_cC^b_{Li^+}D'_{e-Li^+}\right)\left[\frac{1}{\left(1+\dfrac{D'_{e-Li^+}}{k_sRC_{CF_{(s)},0}}\dfrac{r_c}{R}\right)}-\left(1-\dfrac{D'_{e-Li^+}}{k_LR}\right)\left(\dfrac{r_c}{R}\right)\right], \text{(mol/s)}$$ (29)

Corresponding to the shrinking core reaction front at $r = r_c$, the galvanic cell current, in amps, according to the reaction, Eq. (1), per active material particle in the cell cathode during the cell discharge period is given by

$$i^C_{\text{part}} = \left(-\frac{dN_{CF_{(s)}}}{dt}\right)_{\text{part}}\left(\frac{F\left(\begin{array}{c}\text{coulomb of}\\ \text{charge involved}\end{array}\right)}{\begin{array}{c}\text{1 mole of}\\ CF_{(s)} \text{ converted}\end{array}}\right)$$ (30a)

Inserting for $\left(-\dfrac{dN_{CF_{(s)}}}{dt}\right)$ from Eq. (29) into (30a),

$$i_{part}^{C} = \left(4\pi R C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'}\right)\left[\dfrac{\dfrac{r_c}{R}}{1+\dfrac{D_{e-Li^{+}}^{'}}{k_s R C_{CF_{(s)},0}}\dfrac{r_c}{R}} - \left(1-\dfrac{D_{e-Li^{+}}^{'}}{k_L R}\right)\left(\dfrac{r_c}{R}\right)\right] \quad (30b)$$

Inserting for $\left(\dfrac{r_c}{R}\right)$ from Eq. (17) into Eq. (30b),

$$i_{part}^{C} = \left(4\pi R C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'}\right)\left[\dfrac{(1-x)^{1/3}}{1+\dfrac{D_{e-Li^{+}}^{'}}{k_s R C_{CF_{(s)},0}(1-x)^{1/3}}} - \left(1-\dfrac{D_{e-Li^{+}}^{'}}{k_L R}\right)(1-x)^{1/3}\right] \quad (31)$$

For the situation of $D_{e-Li^{+}}^{'} \Box \left(k_s R C_{CF_{(s)},0}\right)$ and $\Box\ (k_L R)$, Eq. (31) reduces to:

$$i_{part\text{-diff}}^{C} = \left(4\pi R C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'}\right)\left[\dfrac{(1-x)^{1/3}}{1-(1-x)^{1/3}}\right] \quad (32)$$

The dimensionless forms of i_{part}^{C} and $i_{part\text{-diff}}^{C}$ are given as:

$$\left[\left(i_{part}^{C}\right)_{d-less}\right] = \left(\dfrac{i_{part}^{C}}{\left(4\pi R C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'}\right)}\right)$$
$$= \left[\dfrac{(1-x)^{1/3}}{1+\dfrac{D_{e-Li^{+}}^{'}}{k_s R C_{CF_{(s)},0}(1-x)^{1/3}}} - \left(1-\dfrac{D_{e-Li^{+}}^{'}}{k_L R}\right)(1-x)^{1/3}\right] \quad (33)$$

$$\left[\left(i_{part-diff}^{C}\right)_{d-less}\right] = \left(\dfrac{i_{part-diff}^{C}}{\left(4\pi R C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'}\right)}\right)$$
$$= \left[\dfrac{(1-x)^{1/3}}{1-(1-x)^{1/3}}\right] \quad (34)$$

Current per unit initial mass of the active material, $CF_{(s)}$, free of 'impurities' in the cathode reactive particle,

$$i_{g-part}^{C} = \dfrac{i_{part}^{C}}{m_{part,0}} \quad (35)$$

where $m_{part,0} = $ initial mass of $CF_{(s)}$ particle $= \dfrac{4}{3}\pi R^3 \rho_{CF_{(s)}}$ and where $\rho_{CF_{(s)}} = $ density of solid $CF_{(s)}$.

Combination of Eq. (31) and (35) results in:

$$i_{g-part}^{C} = \left(\dfrac{3 C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'}}{R^2 \rho_{CF_{(s)}}}\right)\left[\dfrac{(1-x)^{1/3}}{1+\dfrac{D_{e-Li^{+}}^{'}}{k_s R C_{CF_{(s)},0}(1-x)^{1/3}}} - \left(1-\dfrac{D_{e-Li^{+}}^{'}}{k_L R}\right)(1-x)^{1/3}\right] \quad (36)$$

where i_{g-part}^{C} has units of $\left(\text{ampere } g_{part}^{-1}\right)$.

For the case of $D_{e-Li^{+}}^{'} \Box \left(k_s R C_{CF_{(s)},0}\right)$ and $\Box\ (k_L R)$, Eq (36) reduces to:

$$i_{g-part,diff}^{C} = \left(\dfrac{3 C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'}}{R^2 \rho_{CF_{(s)}}}\right)\left[\dfrac{(1-x)^{1/3}}{1-(1-x)^{1/3}}\right] \quad (37)$$

If all the active material, $CF_{(s)}$, particles in the galvanic cell cathode packed-bed have their total initial mass $= m_{part,0}$, [gm]; the total cell cathode current is given by

$$I^{C} = m_{CF_{(s)},0} i_{g-part}^{C}$$
$$= \left(\dfrac{3 C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'} m_{CF_{(s)},0}}{R^2 \rho_{CF_{(s)}}}\right)\left[\dfrac{(1-x)^{1/3}}{1+\dfrac{D_{e-Li^{+}}^{'}}{k_s R C_{CF_{(s)},0}(1-x)^{1/3}}} - \left(1-\dfrac{D_{e-Li^{+}}^{'}}{k_L R}\right)(1-x)^{1/3}\right] \quad (38)$$

For the case of $D_{e-Li^{+}}^{'} \Box \left(k_s R C_{CF_{(s)},0}\right)$ and $\Box\ (k_L R)$, Eq. (38) simplifies to:

$$I_{diff}^{C} = \left(\dfrac{3 C_{Li^{+}}^{b} F D_{e-Li^{+}}^{'} m_{CF_{(s)},0}}{R^2 \rho_{CF_{(s)}}}\right)\left[\dfrac{(1-x)^{1/3}}{1-(1-x)^{1/3}}\right] \quad (39)$$

For the transport and electrochemical reaction processes, in a lithium-based galvanic cell cathode, controlling the

performance behavior, the total cell current, $I_{tot} = I^C$. That is,

$$I_{tot} = I^C$$

$$= \left(\frac{3 C_{Li^+}^b F D_{e-Li^+}' m_{CF_{(s)},0}}{R^2 \rho_{CF_{(s)}}} \right) \left[\frac{(1-x)^{1/3}}{\left(1 + \frac{D_{e-Li^+}'}{k_s R C_{CF_{(s)},0} (1-x)^{1/3}} \right)} - \left(1 - \frac{D_{e-Li^+}'}{k_L R} \right)(1-x)^{1/3} \right] \quad (40)$$

or, for the situation of transport of lithium ions through the solid product layer, surrounding the intrinsic reaction-front, controlling the cell overall discharge,

$$I_{tot,diff} = I_{diff}^C = \left(\frac{3 C_{Li^+}^b F D_{e-Li^+}' m_{CF_{(s)},0}}{R^2 \rho_{CF_{(s)}}} \right) \left[\frac{(1-x)^{1/3}}{1-(1-x)^{1/3}} \right] \quad (41)$$

Now, the effect of shrinking, rapid and extremely thin reaction zone in an active material particle on the current per unit shrinking reaction zone area is explored for the situation of discharge of a lithium/$CF_{(s)}$ cell at a constant current level. For the assumption of identical, spherical active material, $CF_{(s)}$, particles; this implies that the cell current per active material particle must remain invariant throughout the cell discharge period. To express this view in quantitative terms,

$$i_{part}^C = 4\pi R^2 i_{n,R}^C = 4\pi r_c^2 i_{n,r_c}^C = constant \quad (42)$$

or,

$$i_{n,r_c}^C = \left(\frac{i_{part}^C}{4\pi r_c^2} \right) = \left(\frac{i_{part}^C}{4\pi} \right)\left(\frac{1}{r_c^2} \right) \quad (43)$$
$$\left(\frac{ampere}{m^2 \text{ of the intrinsic reaction zone}} \right)$$

From Eq. (43), it is obvious that i_{n,r_c}^C increases proportional to $\left(\frac{1}{r_c^2} \right)$ as r_c decreases. Flux of lithium ions required to arrive at the intrinsic reaction zone surface from the cell electrolytic solution, corresponding to i_{n,r_c}^C, is given by

$$\dot{n}_{Li^+,r_c}^C = \left(\frac{i_{n,r_c}^C}{F} \right) = \left(\frac{i_{part}^C}{4\pi F} \right)\left(\frac{1}{r_c^2} \right) \quad (44)$$
$$\left(\frac{mol \, Li^+}{s \, m^2} \right)$$

With the assumption of the lithium-ion diffusion as the predominant process-controlling mechanism for the rapid reaction shrinking-core model, the lithium-ion molar flux per unit shrinking reaction-zone area is given by

$$\dot{n}_{Li^+,r_c}^C = \left(D_{e-Li^+}' \frac{\partial C_{Li^+-s}'}{\partial r} \bigg|_{r=r_c} \right) \quad (45)$$

where D_{e-Li^+}' = effective lithium-ion diffusivity in the reaction product layer of $\left(LiF_{(s)} + C_{(s)} \right)$ surrounding the unreacted core of $CF_{(s)}$ in the cathode active material particle (see Figure 2) and, C_{Li^+-s}' = lithium-ion molar concentration in the channels of the solid reaction-product layer. Combination of Eq. (44) and (45) leads to:

$$\left(D_{e-Li^+}' \frac{\partial C_{Li^+-s}'}{\partial r} \bigg|_{r=r_c} \right) = \left(\frac{i_{part}^C}{4\pi F} \right)\left(\frac{1}{r_c^2} \right) \quad (46)$$

Inserting for $\left(\frac{\partial C_{Li^+-s}'}{\partial r} \bigg|_{r=r_c} \right)$ from Eq. (6) into Eq. (46) and simplifying:

$$D_{e-Li^+}' \left[\frac{C_{Li^+}^b}{\left[\left(1 + \frac{D_{e-Li^+}'}{k_s C_{CF_{(s)},0} r_c} \right)\left(\frac{1}{r_c} \right) \right] - \left(1 - \frac{D_{e-Li^+}'}{k_L R} \right)\left(\frac{1}{R} \right)} \right] = \left(\frac{i_{part}^C}{4\pi F} \right) \quad (47)$$

For the rapid reaction, shrinking-core situation; with the appropriate assumption of $D_{e-Li^+}' \, \Box \, \left(k_s R C_{CF_{(s)},0} \right)$ as well as $\Box \, \left(k_L R \right)$, Eq. (47) reduces to:

$$D_{e-Li^+}' \left[\frac{C_{Li^+}^b}{\frac{1}{r_c} - \frac{1}{R}} \right] = \left(\frac{i_{part}^C}{4\pi F} \right) \quad (48)$$

Re-expressing Eq. (48) as:

$$D'_{e-Li^+} = \left(\frac{i^C_{part-diff}}{4\pi R C^b_{Li^+} F} \right) \left(\frac{R}{r_c} - 1 \right)$$

$$= \left(\frac{i^C_{part-diff}}{4\pi R C^b_{Li^+} F} \right) \left(\frac{1}{(1-x)^{1/3}} - 1 \right) \tag{49}$$

$$\left(\text{valid} : 0 < x < 1 \text{ and } R > r_c > 0 \right)$$

where the second equality '=' has been obtained using Eq. (17). Equation (49) suggests that D'_{e-Li^+} 'must' increase with the decrease in the radius, r_c, of the active material shrinking core as well as with the increase in the fractional conversion, x, of the active material, $CF_{(s)}$, in the cell cathode if the $\left[Li_{(s)} / CF_{(s)} \right]$ cell is required to be discharged at a constant current level. This required increase in D'_{e-Li^+}, proposed here, is provided by the utilization of some fraction of the cell reaction Gibbs free energy change or by the use of some fraction of available cell voltage. To this end, it is here suggested that a correlation between D'_{e-Li^+} and the cell voltage loss, E_{loss}, be developed from the experimental data acquired on $\left[Li_{(s)} / CF_{(s)} \right]$ cells for at least three temperatures as well as three currents at each temperature for each one of three average active-material, $CF_{(s)}$, particle radii.

III. DATA AND DISCUSSION

Figure 3 shows the plot of the dimensionless time, τ, versus the fractional conversion, x, of the limited solid-state reactant material in the cell cathode, $CF_{(s)}$, during its discharge period in accordance with Eq. (19). Exponential increase in τ as a function of increase in x is quite obvious. This type of plot can be employed to predict the cell discharge time of a lithium/ $CF_{(s)}$ cell as a function of $CF_{(s)}$ fractional conversion provided the data for C^b_{Li}, $C_{CF_{(s)},0}$, R and D'_{e-Li^+} are available. Conversely, from the experimental data on the $CF_{(s)}$ fractional conversion, $x = \left[\left(\frac{I_{tot} M_{CF}}{m_{CF_{(s)},0} F} \right) t \right]$ versus time, t, one can determine D'_{e-Li^+} from Eq. (19) at any t value. Also, one determines the cell voltage-loss, $E_{loss} = \left(E_{OCV} - E \right)$, versus x from the experimental data on a given lithium/ $CF_{(s)}$ cell. Then, one can develop a correlation between the effective lithium-ion diffusivity,

D'_{e-Li^+}, and the cell voltage loss. Such a correlation is represented in Figure 4 using the experimental data from Figure 1(f) [Ref. 4, 6] at $I_{tot} = 16.420 \, mA \, g^{-1}$ of $CF_{(s),x}$, $x = 0.88$, $25\,°C$. The algebraic form of the developed correlation is given below.

$$D'_{e-Li^+} = \begin{pmatrix} -468.0005 + 414.1532 \, E_{loss} \\ -73.2017 E_{loss}^2 - 6.7184 E_{loss}^3 \end{pmatrix} \times 10^{-11} \tag{50}$$

where D'_{e-Li^+} has units of cm²/s and E_{loss} is the cell voltage loss.
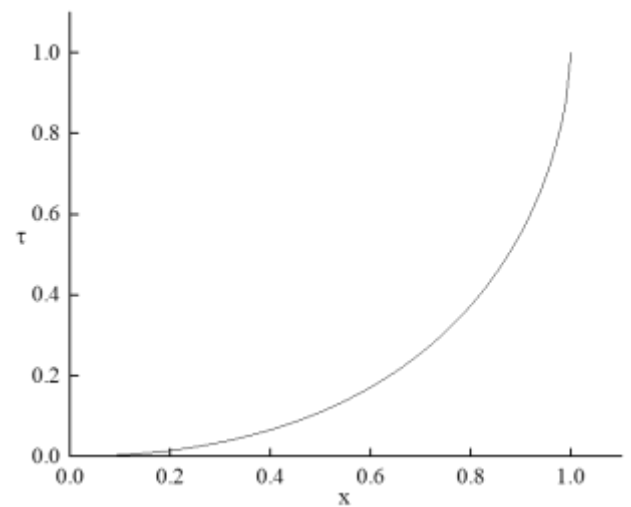

Figure 3: Plot of dimensionless discharge time versus cell cathode active material fractional conversion, x.
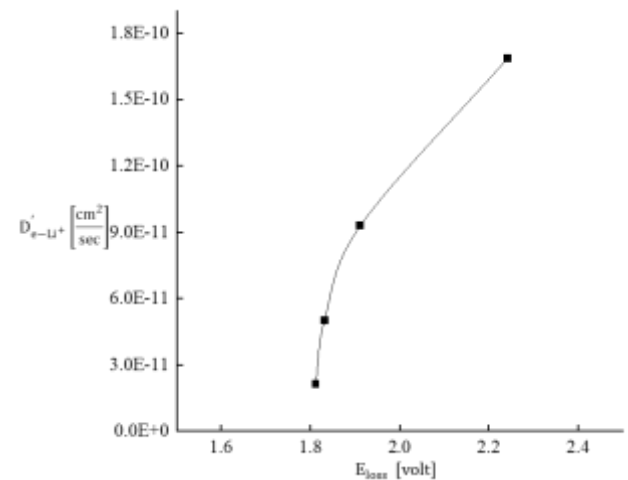

Figure 4: Plot of the lithium-ion effective diffusivity versus the cell voltage loss.

The lithium-ion 'effective diffusivity' obtained from Eq. (50) can be appropriately assumed to account for the resultant effect of [the sum of the resistances to the species (lithium ion and electron) transport in the various cell parts, charge transfer across the cell electrode- electrolyte

interfaces and the cell electrode electrochemical reactions] on the performance behavior, represented in terms of the cell voltage versus time or fractional conversion, x, of $CF_{(s)}$ during the cell discharge period.

Figure 5 shows the predicted speed, S_d (in the dimensionless form), of the reaction zone moving towards the center of an active material $CF_{(s)}$ particle calculated from Eq. (23b) as a function of x. The reaction zone speed, $\dot{r}_c$ is proportional to $\left[\dfrac{D'_{e-Li^+}}{(1-x)^{1/3}-(1-x)^{2/3}} \right]$. It is here noted that as the $CF_{(s)}$ fractional conversion, x, increases; the lithium-ion effective diffusivity in the solid-state active material $CF_{(s)}$ particle is required to increase, as shown in Figure 4, to compensate for the decrease in the reaction zone area in an active material, $CF_{(s)}$, particle at a constant current cell discharge.
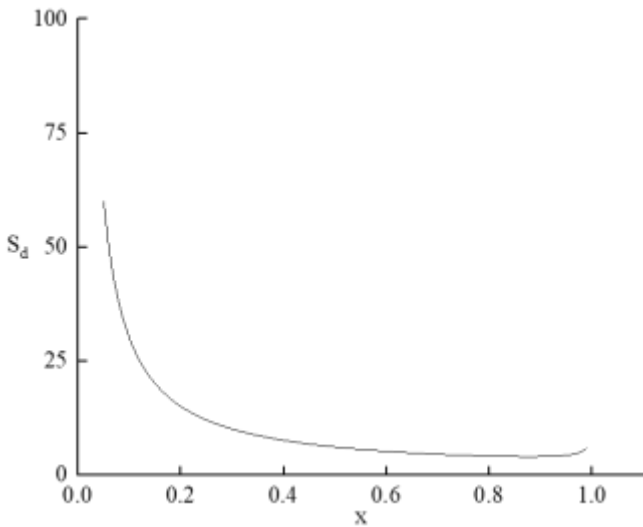
Figure 5: Plot of the dimensionless velocity, S_d, of the moving reaction zone towards the center of a spherical active material particle versus the cell cathode active material fractional conversion, x.

Figure 6 shows the plot of $F(x) = \left[\dfrac{(1-x)^{1/3}}{1-(1-x)^{1/3}} \right]$ versus the fractional conversion of $CF_{(s)}$. Such a plot can be employed to predict the dimensionless currents from the following equation:

$$\left(\frac{4I^{cell}R^2\rho_{CF_{(s)}}}{3C^b_{Li^+}FD'_{e-Li^+}m_{CF_{(s),0}}} \right) = \left(\frac{4I^C_{diff}R^2\rho_{CF_{(s)}}}{3C^b_{Li^+}FD'_{e-Li^+}m_{CF_{(s),0}}} \right)$$

$$= \left(\frac{i^C_{part-diff}}{4\pi RC^b_{Li^+}FD'_{e-Li^+}} \right) = \left(\frac{4i^C_{g-part,diff}R^2\rho_{CF_{(s)}}}{3C^b_{Li^+}FD'_{e-Li^+}} \right) \quad (51)$$

$$= F(x)$$

where

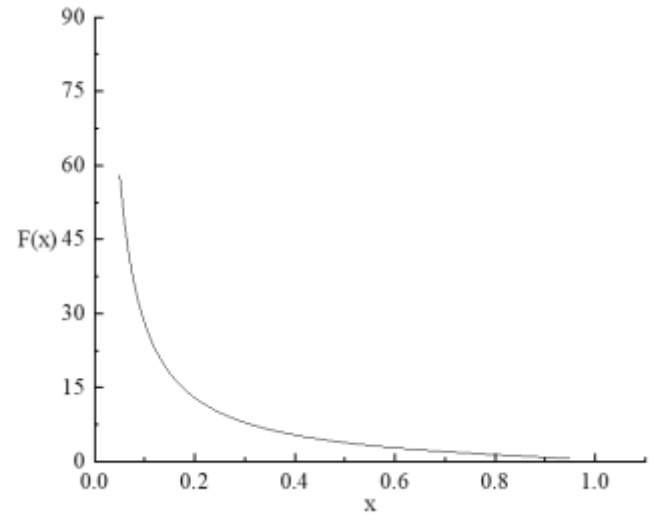$$F(x) = \left[\frac{(1-x)^{1/3}}{1-(1-x)^{1/3}} \right] \quad (52)$$

Figure 6: Plot of the function F(x) versus the cell cathode active material fractional conversion, x.

At any x-value, one can calculate $F(x)$ from Eq. (52) and D'_{e-Li^+} from Eq. (51) for a constant current, I^{cell}, discharge of a given lithium/ $CF_{(s)}$ cell. Inserting the value of D'_{e-Li^+} into Eq. (50), one can determine the cell voltage loss, E_{loss}. Then, the actual cell voltage, $E = E_{OCV} - E_{loss}$ can be computed at that x value, which, in turn, can be used to compute the electric power (W), $\dot{P}_{electric} = I^{cell}E$, at that x value. The total electric energy (J) delivered by the galvanic cell up to the cell discharge time, t (s), corresponding to that x value is given by:

$$E_{electric\ energy} = \int_{'t'=0}^{'t'=t} \dot{P}_{electric}dt = \int_0^t I^{cell}Edt \quad (53)$$

For the constant current cell discharge, I^{cell}, Eq. (53) reduces to:

$$E_{electric\ energy} = \left[I^{cell}\int_0^t Edt \right] \quad (54)$$

The developed formulation shows a linear relation between q_d (the fractional amount of charge involved in the intrinsic electrochemical reaction in the cell cathode) and the cathode active material, $CF_{(s)}$, fractional conversion during the cell discharge period. This relation is represented in Figure 7.
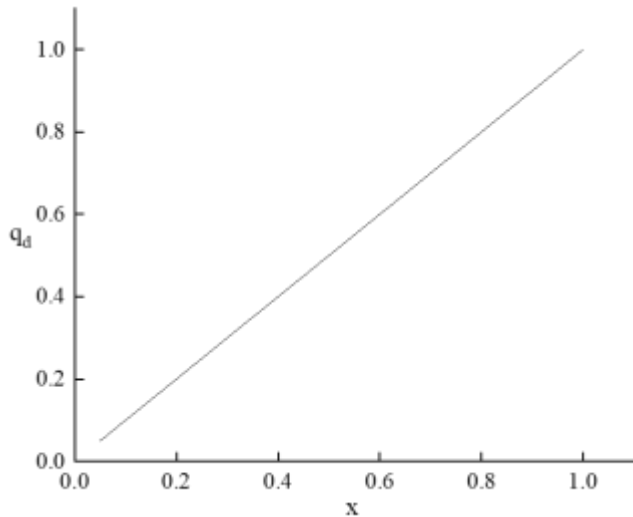

Figure 7: Plot of fractional conversion of charge, q_d, involved in the intrinsic electrochemical reaction in the cell cathode versus the fractional conversion, x, of the cell cathode active material during the cell discharge period.

IV. CONCLUDING REMARKS

To explain the discharge behavior of a lithium/electrolyte/$CF_{(s)}$ galvanic cell; under the condition of lithium-ion diffusion through the microporous solid product layer of $LiF_{(s)}$ for the lithium-ion arrival at the reaction zone of the reaction: $CF_{(s)} + (Li^+ + e^-) \rightarrow LiF_{(s)} + C_{(s)}$, as the predominant mechanism controlling the cell electrochemical behavior, i.e., cell voltage versus time profile; the model formulation presented in this paper was developed. The developed-model formulation links the $CF_{(s)}$ fractional conversion, X, to: (a) the cell discharge time, (b) speed of the moving reaction zone towards the center of a spherical active material particle, (c) fractional amount of charge involved in the cell overall electrochemical reaction, and (d) the cell current. Also, the presented formulation shows that the lithium-ion effective diffusivity must increase with an increase in the $CF_{(s)}$ fractional conversion for the discharge of a lithium/$CF_{(s)}$ cell at a constant current-level. The required enhancement in 'the lithium-ion effective diffusivity' is deemed to be provided at the expense of a fraction of the reaction Gibbs free energy change. Therefore, a correlation between the lithium-ion effective diffusivity and the cell

voltage loss has been developed as an example using the cell discharge data [4].

REFERENCES

1. Sandhu, S. S.; Kosir, S. T.; Fellner, J. P. Thermal energy production and heat exchange between an electrochemical cell and its surroundings. RA J Appl Res. 2021: 07(09): 2497-2502. DOI: 10.47191/rajar/v7i9.03.

2. Sandhu, S. S.; Chen, P.; Fellner, J. P. On the diffusion-controlled transport and accumulation of lithium in an electrode of a lithium-based galvanic cell. RA J Appl Res. 2022: 08(01): 41-46. DOI: 10.47191/rajar/v8i1.08.

3. Froment, G. F.; Bischoff, K.B.; De Wilde, J. Chemical Reactor Analysis and Design. pp. 240-255, (2011, 3rd edition) / John Wiley & Sons, Inc.

4. Ding, Z.; et al. Reaction mechanism and structural evolution of fluorographite cathodes in Li/Na/K batteries. Research Square, July 15, 2020. DOI: 10.21203/rs.3.rs-39097/v1.

5. Newman, J.; Thomas-Alyea, K. E. Electrochemical Systems, p. 7, 212; 2004 (3rd) edition, John Wiley & Sons. Inc.

6. Sandhu, S. S.; Fellner, J. P. Formulation for the Performance Analysis of a Lithium-Carbon Monofluoride Cell. (Manuscript for submission to a journal for publication, February 2023).