



Analysis of an all-solid state (AASS) cell: $LiC_6(s)/Al - \text{doped } LLZO(s)$ electrolyte/ $CoO_2(s)$

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ARTICLE INFO	ABSTRACT
Published Online: 06 October 2026	Based on the fundamental principles of chemical engineering thermodynamics and electrochemical engineering, the formulation was developed for the analysis of the all-solid state electrochemical cell: $LiC_6(s) / Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s) / CoO_2(s)$. The formulation presented in this paper was then used to obtain the analytical data for the determination of the electrochemical performance of this cell. Some of the analytical results are highlighted as follows: 1. The cell open-circuit voltage varies from 3.988 to 3.678 volt over the temperature-variation range from 25 to 250°C. The cell's maximum elective energy delivery efficiency varies from about 91 to 87% over the above given temperature range. The percent ratio of the reversible thermal energy to the total thermal energy involved in the cell's electrochemical reaction varies from about 9.0 to 13.0% over the same temperature range. 2. For the cell electrolyte ($Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s)$) of 10 μm thickness, the ohmic voltage loss varies from 5.0 to 0.1 mV for the cell temperature variation from 25 to 250°C at the geometric current density of $\left(\frac{0.1 mA}{cm^2}\right)$; whereas it is from 10.0 to 0.2 mV at the geometric current density of $\left(\frac{2.0 mA}{cm^2}\right)$ over the above given temperature range. For the cell electrolyte thickness of 20 μm, the ohmic voltage loss variation is from 10.0 to 0.2 mV for the cell temperature variation from 25 to 250°C at the geometric current density of $\left(\frac{0.1 mA}{cm^2}\right)$; whereas at the geometric current density of $\left(\frac{2.0 mA}{cm^2}\right)$, the ohmic voltage loss is from 20.0 to 0.4 mV for same electrolyte thickness of 20 μm and over the same cell operational temperature from 25 to 250°C. 3. At 25°C, the cell cathode activation polarization voltage loss varies approximately from 5 to 100 mV at the geometric current density variation from 0.1 to $\frac{2.0 mA}{cm^2}$. For the same geometric current variation, the cathode activation polarization voltage loss variation is from 0.43 to 8.67 mV at 150°C; 0.18 to 3.52 at 200°C; and 0.09 to 1.72 mV at 250°C. 4. The cell anode activation polarization voltage loss at 25°C varies approximately from 3.4 to 68.2 mV for the cell geometric current density variation from 0.1 to $\frac{2.0 mA}{cm^2}$. For this same range of the geometric current density variation, the cell anode activation polarization voltage loss variation is from 0.1 to 1.2 mV at 150°C; 0.0 to 0.4 mV at 200°C; and 0.0 to 0.2 mV at 250°C. 5. At 25°C, the specific diffusion-induced voltage loss varies from 3.4 to 68.2 mV in the cell anode for the geometric current density variation from 0.1 to $\frac{2.0 mA}{cm^2}$; whereas it is (50 – 150 mV) in the cell cathode at the geometric current density of $\frac{1.0 mA}{cm^2}$ depending on the lithiated state of cobalt oxide in the cell's cathode. 6. At 25°C and the cell's geometric current density of $\frac{1.0 mA}{cm^2}$; the cell operational voltage is 3.7820 volt. At these conditions, the cell actual electric power delivery is found to be equal to $(3.782 \times 10^{-3}) \frac{W}{cm^2}$.
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KEYWORDS: Solid-State Electrochemical Cells, Electrochemical Performance, Thermodynamic Analysis, Electrolyte Conductivity, Polarization Losses, Electric Power Delivery

1. INTRODUCTION

All solid-state batteries such as $LiC_6(s)/Al - \text{doped } LLZO(s)$ electrolyte/ $CoO_2(s)$ as the energy storage systems overcome the energy density limits of conventional lithium-ion batteries and safety hazards. Incombustible solid-state electrolytes are used in all-solid-state batteries (ASSBs) to replace volatile organic liquid electrolytes.

ASSBs can prevent thermal runaway, eliminate leakage risks and allow for the implementation of high-capacity lithium intercalation anodes. The cell architecture:

$LiC_6(s) / Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s) / CoO_2(s)$ represents an ideal cell design that pairs a chemically stable oxide solid electrolyte with a robust intercalation anode and high voltage cathode. The graphite intercalation anode, $LiC_6(s)$, has exceptionally stable voltage profile and low volume expansion compared to pure lithium metal anodes, significantly reducing the mechanical stress exerted on the solid electrolyte during cell cycling.

Lithium lanthanum zirconium oxide ($Li_7La_3Zr_2O_{12}$ or $LLZO$) is highly prominent garnet-type inorganic solid electrolyte due to its high room or ambient – temperature ionic conductivity ($\cong 10^{-3} S \cdot cm^{-1}$) and broad electrochemical stability window. The $Al - \text{doped } LLZO$ stabilizes the highly conductive cubic $C - LLZO$ phase at room temperature and suppresses unwanted phase transitions as well as improves the overall structural stability. Lithium cobalt oxide cathode, $LiCoO_2(s)$, is the positive electrode material in high – energy – density portable electronics. It functions through reversible lithium-ion deintercalation/intercalation process. When completely

delithiated it forms $CoO_2(s)$. It has high volumetric energy density. However, the solid-state implementation requires careful engineering to minimize resistive interactions with the solid electrolyte during high-temperature co-sintering.

Despite the very significant advantages of the $LiC_6(s)/Al - \text{doped } LLZO / CoO_2(s)$ configuration, the electrolyte $Al - \text{doped } LLZO$ exhibit poor physical contact with the solid composite cathodes. This can lead to high interfacial charge-transfer resistance. Traditional high temperature co-sintering of $LLZO$ and cobalt based cathodes frequently leads to thermal degradation and generation of highly resistive phases. Consequently, the battery researchers use novel infiltration or buffer-layer methods. Side reactions or void formation between the negative lithium-metal electrodes and the solid electrolyte can accelerate the cell polarization voltage loss. The use of a structured $LiC_6(s)$ anode helps in the maintenance of mechanical integrity and contact at the interphase with the solid electrolyte better than reactive bare lithium metal.

Section 2, given below, summarizes the relevant formulation employed in the analysis of the all-solid-state cell: $LiC_6(s) / Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s) / CoO_2(s)$.

The cell reactions are:

At the cell anode: $LiC_6(s) \rightleftharpoons Li^+ + e^- + C_6(s)$

(1)

At the cell cathode: $CoO_2(s) + Li^+ + e^- \rightleftharpoons LiCoO_2(s)$

(2)

The overall cell reaction: $LiC_6(s) + CoO_2(s) \rightleftharpoons C_6(s) + LiCoO_2(s)$

(3)

2. RELEVANT FORMULATION

The analytical information provided in this presentation is based on the formulation developed using the engineering and scientific principles given in the references [1-3].

The overall cell reaction, Equation (3), is here expressed as:

$$(-1)LiC_6(s) + (-1)CoO_2(s) + (1)LiCoO_2(s) + (1)C_6(s) = 0 \quad (4)$$

$$\nu_1 = (-1) \quad \nu_2 = (-1) \quad \nu_3 = 1 \quad \nu_4 = 1$$

According to reference[1], the standard-state enthalpy, Gibbs-free energy, and entropy changes for the occurrence of the reaction at cell temperature $T[K]$ are:

$$\Delta H_T^\circ = \Delta H_{T_0}^\circ + R \int_{T_0}^T \left(\frac{\Delta C_p^\circ}{R} \right) dT = \left[\Delta H_{T_0}^\circ + \int_{T_0}^T (\Delta C_p^\circ) dT \right], (J \cdot mol^{-1} \text{ or } kJ \cdot mol^{-1}) \quad (5)$$

$$\left(\frac{\Delta G_T^\circ}{RT} \right) = \left[\frac{\Delta G_{T_0}^\circ - \Delta H_{T_0}^\circ}{RT_0} + \frac{\Delta H_{T_0}^\circ}{RT} + \frac{1}{T} \int_{T_0}^T \left(\frac{\Delta C_p^\circ}{R} \right) dT - \int_{T_0}^T \left(\frac{\Delta C_p^\circ}{RT} \right) dT \right], (dimensionless) \quad (6)$$

$$(\Delta S_T^\circ) = \Delta S_{T_0}^\circ + R \int_{T_0}^T \left[\left(\frac{\Delta C_p^\circ}{R} \right) \frac{1}{T} \right] dT = \left[\Delta S_{T_0}^\circ + \int_{T_0}^T \frac{\Delta C_p^\circ}{T} dT \right], (J \cdot mol^{-1} \cdot K^{-1}) \quad (7)$$

Where

$$\Delta H_{T_0}^\circ = \sum_{j=1}^{j=4} (\nu_j \cdot \Delta H_{f,j,T_0}^\circ) = (-423.6 kJ \cdot mol^{-1} \text{ for the overall cell reaction}),$$

$$\Delta G_{T_0}^\circ = \sum_{j=1}^{j=4} (\nu_j \cdot \Delta G_{f,j,T_0}^\circ) = (-384.75 kJ \cdot mol^{-1} \text{ for the overall cell reaction}),$$

$$\Delta S_{T_0}^\circ = \sum_{j=1}^{j=4} (\nu_j \cdot \Delta S_{f,j,T_0}^\circ) = (-24.3050 J \cdot mol^{-1} \cdot K^{-1} \text{ for the overall cell reaction}),$$

at $T_0 = 25^\circ C \equiv 298.15K$.

$$(\Delta C_p^\circ) = \sum_{j=1}^{j=4} (\nu_j \cdot C_{p,j}), (J \cdot K^{-1} \cdot mol^{-1} \text{ for the overall cell reaction})$$

The standard-state cell voltage at $T = T_0 = 298.15K$ is given by

$$E_{T_0}^{\circ} = \frac{(-\Delta G_{T_0}^{\circ})}{nF}, (volt) \quad (8)$$

where $n = 1 \text{ } g \cdot \text{mole}$ of the unitly-charged particles (Li^+, e^-) involved per $g \cdot \text{mole}$ of the overall cell reaction, Equation (3), occurring; $F = \text{Faraday constant} = 96487.0 \text{ coulombs}$ $\left[\frac{(g - \text{equivalent})^{-1} \text{ or}}{(g - \text{mole of the unitly charged particles})^{-1}} \right]$.

The cell electric potential $E_{T_0}^{\circ}$ is also termed as the cell open-circuit electric potential at temperature $T_0 = 298.15K (= 25^{\circ}C)$, with the species involved in the overall cell reaction in their respective standard-states.

If the activities of the species involved in the cell reaction differ from unity; then,

$$\Delta G_T = \Delta G_T^{\circ} + RT \ln \left[\prod_j a_j^{v_j} \right], (J \cdot \text{mol}^{-1}), \quad (9)$$

Dividing by $(-nF)$,

$$\text{and } E_T = E_T^{\circ} - \frac{RT}{nF} \ln \left[\prod_j a_j^{v_j} \right], (volt). \quad (10)$$

(for the overall cell reaction, Equation (3) or (4), $n = 1$); Also, if activity of each species involved, $a_j = 1$; then, $\Delta G_T = \Delta G_T^{\circ}$ and $E_T = E_T^{\circ}$.

$R = \text{the universal gas constant} = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot K^{-1}$.

The cell electric potential, E_T , is also called the cell's open-circuit electric potential for the cell operational case, when a_j 's are not equal = 1.

The reversible thermal energy production per mole of the reaction Equation (3) occurring at the cell temperature of $T[K]$ is given by $q_{reversible,T}^{\circ} = (T \cdot \Delta S_T^{\circ})$,

$$(J \cdot \text{mol}^{-1} \text{ of the reaction, Equation (3), occurring during the cell discharge period}). \quad (11)$$

Maximum efficiency of the cell to produce electric energy at $T[K]$ is given by

$$\eta_{max,electric,T}^{\circ} = \frac{\Delta G_T^{\circ}}{\Delta H_T^{\circ}} \quad (12)$$

$$\text{Also, at } T = T_0[K], \eta_{max,electric,T_0}^{\circ} = \frac{\Delta G_{T_0}^{\circ}}{\Delta H_{T_0}^{\circ}} \quad (13)$$

The fraction of the reaction thermal energy appearing as the reversible heat (which must be removed to maintain the desired cell temperature, $T[K]$) is: $f_{reversible \text{ heat},T} = \frac{q_{reversible,T}^{\circ}}{\Delta H_T^{\circ}} = \frac{T \Delta S_T^{\circ}}{\Delta H_T^{\circ}}$ (14)

$$\text{At } T = T_0[K], f_{reversible \text{ thermal energy},T_0} = \frac{T_0 \Delta S_{T_0}^{\circ}}{\Delta H_{T_0}^{\circ}} \quad (15)$$

During the cell discharge period, the ohmic voltage loss associated with the lithium-ion transport through a solid-state electrolyte such as the aluminum-doped $LLZO, Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s)$, can be calculated from

$$\Delta V_{\Omega,electrolyte} = \frac{i_{geom} t_{s-electrolyte}}{\sigma_{s-electrolyte}}, (volt) \quad (16)$$

where $i_{geom} = \text{geometric current density, } (A \cdot cm^{-2})$;

$t_{s-electrolyte} = \text{thickness of the solid electrolyte membrane between the cell anode and cathode electrodes (cm)}$ and $\sigma_{s-electrolyte} = \text{the ionic conductivity of the electrolyte separator, } \left(\frac{S}{cm} = \frac{1}{ohm \cdot cm} = ohm^{-1} cm^{-1} \right)$.

The Butler-Volmer equation relates the current density at the interface between the solid electrolyte and an electrode (e.g., here the cell cathode) to the electrode reaction overvoltage, η_S^C , as given below,

$$i^C = i_0^C \left[\exp \left\{ \frac{(1-\beta^C)nF}{RT} \eta_S^C \right\} - \exp \left\{ \frac{-\beta^C nF}{RT} \eta_S^C \right\} \right], (amp \cdot m^{-2} \text{ or } amp \cdot cm^{-2}) \quad (17)$$

For the reaction, Equation (2), here, $n = 1$ (i.e., 1 mole of electrons are involved in the reaction occurring at the cell cathode; therefore, Equation (17) reduces to:

$$i^C = i_0^C \left[\exp \left\{ \frac{(1-\beta^C)F\eta_S^C}{RT} \right\} - \exp \left\{ \frac{\beta^C F(-\eta_S^C)}{RT} \right\} \right], (amp \cdot m^{-2} \text{ or } amp \cdot cm^{-2}) \quad (18)$$

I
II

where $\beta^C = \text{called the symmetry factor for the reaction, Equation (2), occurring at the cell cathode, } i_0^C = \text{exchange current density, } (A \cdot m^{-2} \text{ or } A \cdot cm^{-2})$;

noting that $i_0^C = i_0^C(T, a_j; j = Li^+ \text{ in the solid electrolyte solid cobalt oxide, or solid lithium cobalt oxide})$ where $a_j = \text{activity of a species } j$, indicative of its molar concentration in its respective phase. The rate of the electrochemical reaction occurring in the cell cathode is represented as:

$$\left(\frac{i^C}{F} \right) = \left(\frac{i_0^C}{F} \right) \left[\exp \left\{ \frac{(1-\beta^C)F\eta_{S-act}^C}{RT} \right\} - \exp \left\{ \frac{\beta^C F(-\eta_{S-act}^C)}{RT} \right\} \right], \left(\frac{\text{moles of the reaction (2) occurring}}{\text{sec} \cdot cm^2 \text{ of the interfacial area between the cathode and electrolyte}} \right) \quad (19)$$

For a cell such as: $LiC_6(s) / Al - doped LLZO, Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s) / CoO_2(s)$; the exchange current density $i_{0,T}^C$ at any temperature can be calculated from the following Arrhenius type relation:

$$i_{0,T}^C = i_{0,298}^C e^{\frac{E^C}{k_B}(\frac{1}{298.15} - \frac{1}{T})}, (A \cdot m^{-2}) \quad (20)$$

where E^c = activation energy for the reaction occurring at the cathode of the above given cell = 0.35 eV (a typical value) and k_B = the Boltzmann constant = $8.620 \times 10^{-5} \frac{\text{eV}}{\text{K}}$. Equation (20) is further simplified to:

$$i_{0,T}^C = i_{0,298}^C \exp \left[4060.3248 \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \quad (21)$$

where $i_{0,298}^C = 1.5 \text{ A} \cdot \text{m}^{-2} = 0.15 \text{ mA} \cdot \text{cm}^{-2}$, the exchange current density at $25^\circ\text{C} \equiv 298.15\text{K}$ for the occurrence of the reaction at the cell cathode electrode where lithium ions are reduced during the cell discharge period. Similarly, for the occurrence of the reaction at the cell anode, $\text{LiC}_6(s)$, the exchange current density at a temperature $T[\text{K}]$ can be calculated from:

$$i_{0,T}^A = i_{0,298}^A \exp \left[\frac{E_a}{k_B} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \quad (22)$$

where E_a = the reaction activation energy = 0.40 eV (a typical value) and $\frac{E_a}{k_B} = 4640.3712$ K. So, re-expressing Equation (22) as:

$$i_{0,T}^A = i_{0,298}^A \exp \left[4640.3712 \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \quad (23)$$

where the exchange current density at 298.15K is:

$$i_{0.298}^A = 3.0 \text{ A} \cdot \text{m}^{-2} (= 0.3 \text{ mA} \cdot \text{cm}^{-2}).$$

The Butler-Volmer equation at the cell's anode electrode appears as:

$$i^A = i_0^A \left[\underset{\text{I}}{\exp \left\{ \frac{(1-\beta^A)F\eta_S^A}{RT} \right\}} - \underset{\text{II}}{\exp \left\{ \frac{\beta^A F(-\eta_S^A)}{RT} \right\}} \right], (\text{amp} \cdot \text{m}^{-2}) \quad (24)$$

It is here recognized that during the cell discharge period, at high current levels, term I is much greater than term II in Equation 24, whereas term II is much greater than term I in Equation 18. The current density at the cell's anode has positive sign whereas the current density at the cell's cathode has negative sign according to the sign convention. However, the total current at the cell's anode is equal to the total current at the cell's cathode in magnitude; i.e., $(i^A \times a_{tot}^A) = (|i^C| \times a_{tot}^C)$

(25) where a_{tot}^A, a_{tot}^C = total geometric surface area of the anode and cathode electrode, respectively, and $|i^C|$ = magnitude of the current density at the cell's cathode electrode.

For the low overpotential, $|\eta_s^C|$, values; Equation (17) is expanded using the Maclaurin series [4]:

$$i_c = i_0^C \left[\left\{ 1 + \frac{(1-\beta^C)n_F}{RT} n_S^C + \text{higher terms being omitted because they are very small} \right\} - \left\{ 1 + \frac{(-\beta^C n_F \eta_S^C)}{RT} + \text{higher terms omitted} \right\} \right] \quad (26)$$

$$= i_0^C \left(\frac{nF\eta_S^C}{RT} \right) \quad (27)$$

$$\text{For the case here, } n = 1; \text{ therefore, } i_C = i_0^C \left(\frac{F\eta_S^C}{RT} \right) \quad (28)$$

To represent the current at the cell cathode at a temperature $T[K]$ during the cell discharge period, $\eta_S^C = (V^C - E_T^C)$; (volt) is negative.

Therefore, the geometric current density i_c is negative during the cell discharge period. Equation (27) or one similar to this equation is frequently used when the overpotential $|\eta_S^C|$ is 10 mV or less [3].

The use of Equation (17) is somewhat inconvenient because its solution for the determination of η_S^C is laborious. For the special case where the charge transfer coefficient; $(1 - \beta^C)[= \alpha_a^C] = \beta^C (= \alpha_c^C) = \alpha^C$; Equation (17) becomes:

$$i^C = i_0^C \left[e^{\left(\frac{\alpha^C n^C}{RT} \eta_S^C \right)} - e^{-\left(\frac{\alpha^C n^C}{RT} \eta_S^C \right)} \right] \quad (29)$$

$$i^C = i_0^C \left[2 \sinh \left\{ \frac{\alpha^C n_F}{RT} \eta_S^C \right\} \right]; [4]$$

$$i^C = 2i_0^C \sinh\left(\frac{\alpha_{nF}^C}{RT} \eta_S^C\right) \quad (30)$$

For the cell reaction being treated here, $n = 1$; therefore, Equation (30) is expressed as:

$$i^C = 2i_0^C \sinh\left(\frac{\alpha_F^C}{p_T} \eta_S^C\right) \quad (31)$$

For the case of $(-\eta_{\xi}^C)$ large and positive or η_{ξ}^C is negative but large in its magnitude value, Equation (29) reduces to

$$i^C = (-i_0^C) e^{\left(\frac{\alpha^C n F}{RT}\right)(-\eta_S^C)} \quad (32)$$

$$\text{Or } \left[\frac{-i^C}{i_0^C}\right] = e^{\frac{\alpha^C n F}{RT}(-\eta_S^C)} \quad (33)$$

$$\text{Or } \left[\frac{|i^C|}{i_0^C}\right] = e^{\left(\frac{\alpha^C n F}{RT}\right)(-\eta_S^C)} \quad (34)$$

This is the Tafel equation for the cathodic direction reaction at the cell cathode during the period of the cell discharge.

Here $(-\eta_S^C) = (E_T^C - V^C)$; (volt), where E_T^C = the open circuit electric potential at the cell cathode and V^C = the operational electric potential at the cell cathode during the time period the electric power is being delivered by the cell to an external load. For the cell being treated here, $n = 1$; therefore, Equation (34) is expressed as:

$$\left(\frac{|i^C|}{i_0^C}\right) = e^{\frac{\alpha^C F}{RT}(-\eta_S^C)} \quad (35)$$

This Tafel approximation is used when the activation polarization (i.e., voltage loss relative to the open-circuit electrode potential) is at least in the range of (50 – 100 mV).

Equation (34) can also be rearranged in the following forms:

$$|\eta_S^C| = \left(\frac{RT}{\alpha^C F}\right) \ln \left(\frac{|i^C|}{i_0^C}\right) \quad (36)$$

$$= \left(\frac{2.303RT}{\alpha^C F}\right) \log_{10} \left(\frac{|i^C|}{i_0^C}\right) \quad (37)$$

$$= (-a) + b \log_{10} |i^C| \quad (38)$$

$$\text{where } a = \left(\frac{2.303RT}{\alpha^C F}\right) \log_{10} i_0^C, (\text{volt}) \quad (39)$$

$$b = \left(\frac{2.303RT}{\alpha^C F}\right), (\text{volt}). \quad (40)$$

The constant 'b' is called the Tafel slope. When the current density $|i^C|$ increases by a factor of 10, the overpotential due to the reaction polarization at the cathode electrode increases by b volts. At 25°C, $\left(\frac{2.303RT}{F}\right)$ is equal to (0.0592 volt). Usually α^C value is between 0.2 and 2. So, the Tafel slope b varies between 29.6 and 296.0 mV per decade (i.e. per change in $|i^C|$ by a factor of 10). The values for the Tafel slope b and exchange current density i_0^C are often obtained as an empirical fit to the experimental data. While acquiring the experimental data to obtain the Tafel slope b and the exchange current density i_0^C , one should take precaution to eliminate non-kinetic effects, e.g., mass transport limitations.

The lithium graphite, $LiC_6(s)$, is a highly conductive metallic graphite intercalation compound. Its baseline electrical conductivity, in the basal plane (parallel to the graphene layers in the graphite), is very high, typically around $(2 \rightarrow 3) \times 10^5 \left(\frac{S}{cm}\right)$ at 25°C; which is comparable to that of many pure metals, e.g., approx. $3.5 \times 10^5 \left(\frac{S}{cm}\right)$ of aluminum, Al (annealed). Because $LiC_6(s)$ behaves like a metal. Consequently, its electrical conductivity decreases as temperature increases and increases at colder temperatures. This is because of the enhanced electron-phonon (interaction related) scattering at higher material temperatures. Electric conductivity of $LiC_6(s)$ is highly anisotropic, i.e., it is not the same in all directions. For example, its electric conductivity along C-axis (perpendicular to the basal plane parallel to the graphene layers) is very significantly lower and it behaves more like a semiconductor. The molar concentration of mobile lithium ions in $LiC_6(s)$ is: $(28.3 \rightarrow 31.0) \times 10^3 (mol \cdot m^{-3})$.

The delithiated $CoO_2(s)$ has a metallic-like conductivity. It ranges from 10^2 to $10^4 \left(\frac{S}{cm}\right)$ at 25°C. The lithiated cobalt oxide, $Li_{1-x}CoO_2(s)$, has its electrical conductivity dependent on the degree of lithiation (i.e., g-atoms of lithium per g-mole of CoO_2) and the cell cathode's operational temperature. For the delithiated state, $CoO_2(s)$, the material is degenerate and has metallic-like conductivity. With increase in temperature, its electrical conductivity decreases slightly (i.e., its resistivity increases with an increase in temperature due to the enhanced electron-phonon interaction-related scattering). When the material is in the partially lithiated state (e.g., $Li_{0.5}CoO_2(s)$), it behaves as a small-polaron* semiconductor. The electrical conductivity is thermally activated and increases with an increase in the material temperature, following the Arrhenius-like relation

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (41)$$

where k_B = Boltzmann constant = $8.620 \times 10^{-5} \left(\frac{eV}{K}\right)$, E_a = activation energy, (eV). When the material is in the $LiCoO_2(s)$ state, it behaves like a semiconductor with large energy band gap of approximately 1.15 eV. The bulk $CoO_2(s)$ in its pure form is highly metastable. At the elevated temperatures above 300 – 350°C; the delithiated cathode material, $CoO_2(s)$, begins to decompose, losing oxygen and often transforming into intermediate phases such as $Co_3O_4(s)$ or $CoO(s)$. This structural breakdown degrades the overall electronic transport in practical cell or battery operations.

*A small-polaron (a charge conducting electron): It is a quasi-particle when an [electron (hole)] pair is trapped in a crystal lattice because of energetically strong electron-phonon interactions. The charge carrier, e^- , digs its own potential energy well by severely distorting the surrounding atoms in the material lattice. The charge carrier moves through the material from one site to next in the material lattice via the thermally activated hopping (jumping) process. The electrical conductivity in $CoO_2(s)$ material or such a similar material is highly governed by the small-polaron hopping mechanism. It is also here noted that a phonon is imagined as a quantum of thermal vibrational or sound energy.

The molar concentration of the cathode material in the state of the completely delithiated state, $CoO_2(s)$, is $(51.7452 \times 10^3 \text{ mol} \cdot m^{-3})$. So, the molar concentration of lithium in the cathode material in the state of $LiCoO_2(s)$ is $(51.7452 \times 10^3 \text{ mol of lithium} \cdot m^{-3})$. Therefore, the molar concentration of lithium in the partially lithiated, $Li_xCoO_2(s)$, state of the cell cathode material is given by

$$C_{Li^+} = x C_{max} \quad (42)$$

$$\text{where } C_{max} = C_{Li^+,max} = 51.7452 \times 10^3 \text{ mol} \cdot m^{-3} \quad (43)$$

Diffusivity of lithium ions as a function of temperature in the cell cathode is given by

$$[D_{Li}(at T)] = D_0(x) \exp\left(-\frac{E_a(x)}{k_B T}\right), \quad (44)$$

where E_a = (lithium-ion diffusion-related activation energy)

$$= (0.30 \text{ to } 0.75 \text{ eV}); \text{ it is } 0.30 \text{ eV} \text{ when the cathode is in } CoO_2(s) \text{ state and } 0.75 \text{ eV} \text{ when it is in } LiCoO_2(s) \text{ state,}$$

$D_0(x)$ = pre-exponential factor; its value depends on the lithium concentration in the cathode state in the form of $Li_xCoO_2(s)$, k_B = Boltzmann constant = $\left(8.617 \times 10^{-5} \frac{eV}{K}\right)$ and T = absolute temperature [K].

When x [in $Li_xCoO_2(s)$] increases towards one, (the cathode material is in the form of $LiCoO_2(s)$), fewer and fewer interstitial vacant sites result in higher and higher activation energy $E_a(x)$. Consequently, the lithium diffusivity decreases with an increase in x – value at the same temperature of the cell cathode. At $x \approx 0.5$ (ordered phase), the lithium-ordering in $CoO_2(s)$ results in a local minimum in the chemical diffusion coefficient. At room temperature of $25^\circ C = 298.15 K$; D_{Li^+} is between 10^{-12} to $10^{-14} (m^2 \cdot s^{-1})$. Typically, $D_0(x)$ is on the order of 10^{-7} to $10^{-9} (m^2 \cdot s^{-1})$ for $x = 0$ to 1.

The fundamental Nernst-Einstein equation relates the lithium conductivity with its diffusivity in the cell cathode material in the state of $Li_xCoO_2(s)$ as follows:

$$[\sigma_{Li^+}(T, x)] = \frac{F^2 C_{Li^+}(x) D_{Li^+}(at T)}{RT}, \left(\frac{1}{ohm \cdot m}\right), [Li^+, z_+ = +1] \quad (45)$$

$$\text{where } [C_{Li}(x)] = x C_{Li^+,max} = x(51.7452 \times 10^3), (mol \cdot m^{-3}), \quad (46)$$

$$R = 8.314 \frac{J}{mol \cdot K} = \frac{8.314(Coulomb \cdot volt)}{mol \cdot K}.$$

The lithium-ion diffusivity in the cell separator, electrolyte ($Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s)$) is given by the following Arrhenius type equation:

$$D_{Li^+}(T) = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (47)$$

where D_0 = pre-exponential factor has its value of $(10^{-8} \rightarrow 10^{-7})(m^2 \cdot s^{-1})$,

$$k_B = (\text{Boltzmann Constant}) = \left(8.617 \times 10^{-5} \frac{eV}{K}\right),$$

E_a = diffusion related activation energy for the lithium-ion diffusion in the electrolyte separator = $(0.25 \rightarrow 0.45) eV$ depending on the amount of aluminum in the electrolyte; $E_a = 0.25 \text{ eV}$ when the amount of aluminum doped into $[LLZO(Li_7La_3Zr_2O_{12}(s))]$ is zero and $E_a = 0.45 \text{ eV}$ in $[Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s)]$. Note that $1 eV = 1.60 \times 10^{-19} J = 1.60 \times 10^{-19} (coulomb \cdot volt)$.

At room temperature of $25^\circ C$, $D_{Li^+,T_0} = (10^{-11} \rightarrow 10^{-13}) m^2 \cdot s^{-1}$,

where $T_0 = 298.15 K$.

The relation between $D_{Li^+}(at T)$ and $D_{Li^+}(at T_0)$ is

$$[D_{Li^+}(T)] = [D_{Li^+}(at T_0)] \exp\left[\frac{E_a}{k_B} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad (48)$$

The lithium-ion conductivity in the electrolyte, $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s)$, is given by the Nernst-Einstein relation,

$$\sigma_{Li^+} = \frac{n_{Li^+} (q_{Li^+})^2 D_{Li^+}(at T)}{(k_B T)}, \left(\frac{s}{cm}\right) \quad (49)$$

where

n_{Li^+} = number density of Li^+ ions in the electrolyte separator

“Analysis of an all-solid state (AASS) cell: $LiC_6(s)/Al - \text{doped } LLZO(s) \text{ electrolyte/ } CoO_2(s)$ ”

$$\cong (2.56 \times 10^{22} \text{ of } Li^+ \text{ ions}) \text{ or } (0.0425 \text{ mol of } Li^+ \text{ ions}) \text{ cm}^{-3} \text{ of solid, } Li_7La_3Zr_2O_{12}(s),$$

$$\cong (2.28 \times 10^{22} \text{ of } Li^+ \text{ ions}) \text{ or } (0.0378 \text{ mol of } Li^+ \text{ ions}) \text{ cm}^{-3} \text{ of solid,}$$

$$Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s),$$

$$q_{Li^+} = (\text{charge on } Li^+ \text{ ion}) = |e| = (\text{magnitude of charge on an electron})$$

$$= (1.602 \times 10^{-19} \text{ C}); \text{ noting } C \text{ stands for coulomb.}$$

$$k_B (= \text{Boltzmann Constant}) = \left(8.617 \times 10^{-5} \frac{eV}{K}\right); (\text{noting } (1 \text{ eV}) = 1.6 \times 10^{-19} \text{ J} = 1.6 \times 10^{-19} \text{ C.V.}).$$

Note: The total ionic conductivity = $4.0 \times 10^{-4} \frac{S}{cm}$, (for dense, hot-pressed solid).

For unsintered, cold-pressed powder pellets, the conductivity ranges from 10^{-5} to $10^{-4} \frac{S}{cm}$.

The total Li^+ ion concentration remains practically constant across different operational temperatures because the crystal structure of the electrolyte remains fixed.

For the $\mathcal{D}_0$ value of $(5.5 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1})$ and

$$E_a = \frac{(0.25+0.45)eV}{2} = 0.35eV, \mathcal{D}_{Li^+, T_0} \cong (8.35 \times 10^{-14}) (\text{m}^2 \cdot \text{s}^{-1}) \text{ using Equation (47).} \quad (50)$$

For the unsintered cold-pressed powder pellets, the conductivity ranges from 10^{-5} to $10^{-4} \frac{S}{cm}$. It is almost ionic transport. The electronic charge transport in $(Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s))$ used as the solid electrolyte is less than the ionic charge transport by a factor of 10^4 .

3. THE CALCULATED DATA AS WELL AS THAT COMPILED FROM THE LITERATURE RELEVANT TO THE CELL: $LiC_6(s) / Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s) / CoO_2(s)$

The formulation presented in Equation (1) through (15) was used to calculate the data presented in Table 1 given below.

Table 1: Thermodynamic-based calculated data

Temperature		$E_T^{\circ}(\text{volt})$ open-circuit cell voltage	ΔH_T° ($J \cdot \text{mol}^{-1}$) of the reaction	ΔG_T° ($J \cdot \text{mol}^{-1}$) of the reaction	$\eta_{\max, \text{electric}} = \left(\frac{\Delta G_T^{\circ}}{\Delta H_T^{\circ}}\right)$	$q_{r,T}^{\circ} = (T\Delta S_T^{\circ})$ ($J \cdot \text{mol}^{-1}$) of the reaction reversible heat	$F_{\text{reversible-thermal}} = \left(\frac{T\Delta S_T^{\circ}}{\Delta H_T^{\circ}}\right)$ (reversible-heat fraction of the total cell thermal energy produced)
$^{\circ}\text{C}$	K						
25	298.15	3.9876	-423.6×10^3	-384.7500×10^3	0.91	-38.85×10^3	0.092
150	423.15	3.7291	-413.9738×10^3	-359.8050×10^3	0.87	-54.1688×10^3	0.131
200	473.15	3.7230	-410.2144×10^3	-359.2166×10^3	0.87	-50.947×10^3	0.124
250	523.15	3.6777	-406.4334×10^3	-354.8464×10^3	0.87	-51.587×10^3	0.127

Table 2 shows the ohmic voltage drop for the solid electrolyte of the cell, $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s)$, calculated using Equation (16) and the pragmatic ionic conductivity values at different temperatures. It is also here noted that the crystal structure of the aluminum-doped $LLZO(s)$ is that of the cubic (garnet) phase.

Table 2: The cell ohmic voltage drop in the cell electrolyte, $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}(s)$.

T-2-A: Thickness of the solid electrolyte, $t_{s-\text{electro}} = 10 \mu\text{m} = 10^{-3} \text{ cm}$:

T-2-A-1: Geometric current density, $i_{\text{geom}} = 1 \text{ mA} \cdot \text{cm}^{-2} = 10^{-3} \text{ A} \cdot \text{cm}^{-2}$

Temperature		Pragmatic electrical conductivity, $\sigma_{s-\text{electro}}$ ($S \cdot \text{cm}^{-1} = \Omega^{-1} \cdot \text{cm}^{-1}$)	Ohmic voltage drop in the electrolyte, $\Delta V_{\Omega, \text{electro}}(\text{mV})$
$^{\circ}\text{C}$	K		
25	298.15	$2.0 \times 10^{-4} = 0.2 \times 10^{-3}$	5
150	423.15	3.0×10^{-3}	0.3333
200	473.15	6.0×10^{-3}	0.1668
250	523.15	10^{-2}	0.1000
Note: For dense pellets $\sigma_{s-\text{electro}} \cong 4 \times 10^{-5} \frac{S}{cm}$.			

T-2-A-2: Geometric current density, $i_{geom} = 2 \text{ mA} \cdot \text{cm}^{-2} = (2 \times 10^{-3}) \text{ A} \cdot \text{cm}^{-2}$

Temperature °C	T K	electrolyte conductivity, ($S \cdot \text{cm}^{-1} = \Omega^{-1} \cdot \text{cm}^{-1}$)	electrical $\sigma_{s-electro}$ ($S \cdot \text{cm}^{-1} = \Omega^{-1} \cdot \text{cm}^{-1}$)	Ohmic voltage drop in the electrolyte, $\Delta V_{\Omega,electro}(\text{mV})$
25	298.15	0.2×10^{-3}		10
150	423.15	3.0×10^{-3}		0.6666
200	473.15	6.0×10^{-3}		0.3334
250	523.15	10×10^{-3}		0.2000

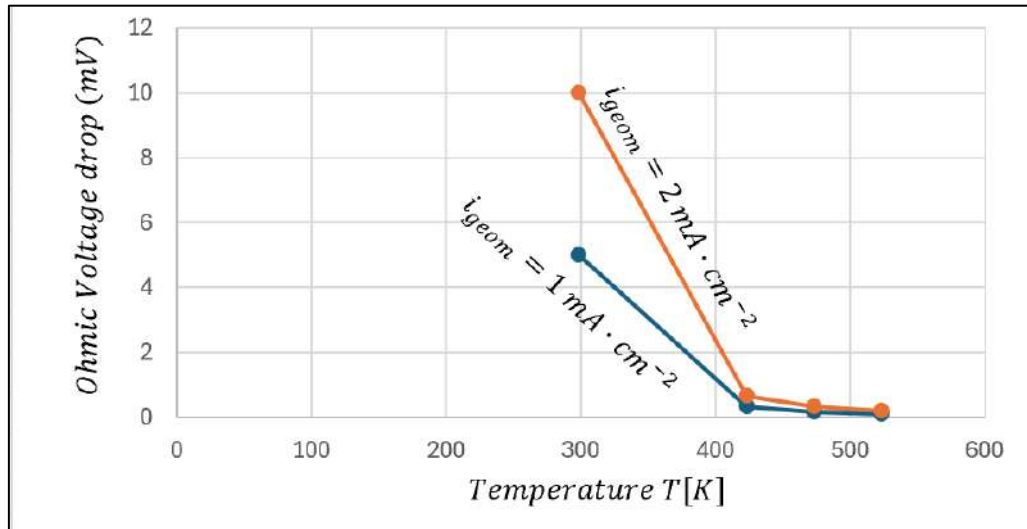


Figure 1: Ohmic Voltage drop (mV) vs. Temperature $T[\text{K}]$, Electrolyte thickness, $t_{s-electro} = 10 \mu\text{m}$.

T-2-B: The solid electrolyte thickness, $t_{s-electro} = 20 \mu\text{m} = 2 \times 10^{-3} \text{ cm}$

T-2-B-1: $i_{geom} = 1 \text{ mA} \cdot \text{cm}^{-2} = 1 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}$

Temperature °C	T K	electrolyte conductivity, ($S \cdot \text{cm}^{-1} = \Omega^{-1} \cdot \text{cm}^{-1}$)	electrical $\sigma_{s-electro}$ ($S \cdot \text{cm}^{-1} = \Omega^{-1} \cdot \text{cm}^{-1}$)	Ohmic voltage drop in the electrolyte, $\Delta V_{\Omega,electro}(\text{mV})$
25	298.15	0.2×10^{-3}		10
150	423.15	3.0×10^{-3}		0.6666
200	473.15	6.0×10^{-3}		0.3336
250	523.15	10×10^{-3}		0.2000

T-2-B-2: Geometric current density, $i_{geom} = 2 \text{ mA} \cdot \text{cm}^{-2} = 2 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}$

Temperature °C	T K	electrolyte conductivity, ($S \cdot \text{cm}^{-1} = \Omega^{-1} \cdot \text{cm}^{-1}$)	electrical $\sigma_{s-electro}$ ($S \cdot \text{cm}^{-1} = \Omega^{-1} \cdot \text{cm}^{-1}$)	Ohmic voltage drop in the electrolyte, $\Delta V_{\Omega,electro}(\text{mV})$
25	298.15	0.2×10^{-3}		20
150	423.15	3.0×10^{-3}		1.3332
200	473.15	6.0×10^{-3}		0.6672
250	523.15	10×10^{-3}		0.4000

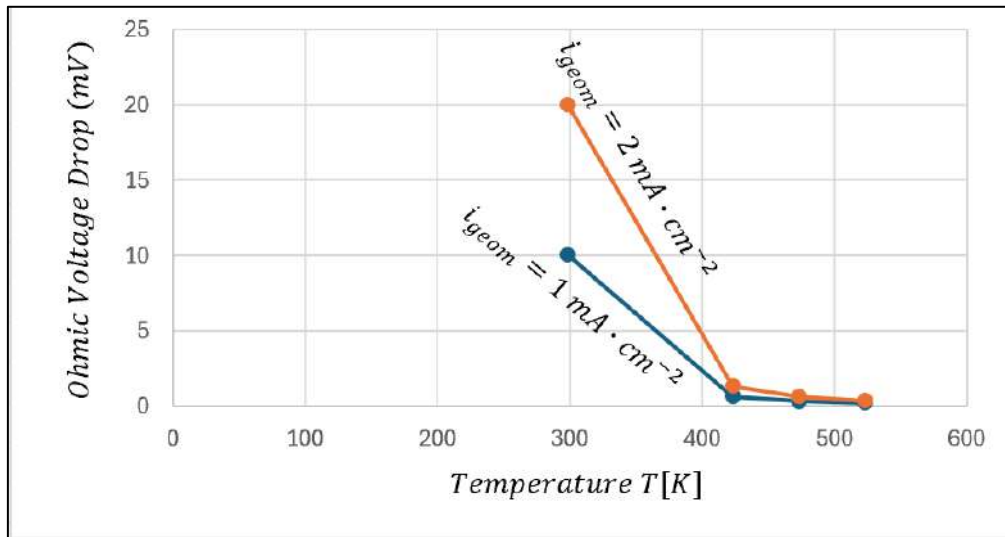


Figure 2: Ohmic Voltage drop (mV) vs. Temperature $T[K]$, Electrolyte thickness, $t_{s-electro} = 20\mu\text{m}$.

The activation polarization voltage loss due to the occurrence of the reaction, Equation (2), in the net cathodic direction is strongly governed by the charge-transfer kinetics and the interfacial contact resistance between the cell cathode $CoO_{2(s)}$ and its electrolyte, $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98(s)}$. At the low activation polarization potentials, the activation polarization voltage loss $|\eta_{S-act}^c|$ is proportional to the current density and the charge transfer resistance, $R_{ct(\Omega)}$. The linearized form of the Butler-Volmer equation leads to:

$$|\eta_{S-act}^c| = iR_{ct}, (\text{volt}) \quad (51)$$

here the charge transfer, area specific resistance, R_{ct} , is given by:

$$R_{ct} = \left(\frac{RT}{Fi_{0,T}^c} \right), (\Omega \cdot \text{cm}^2) \quad (52)$$

where $i_{0,T}^c$ = exchange current density at the cell temperature $T[K]$. With the assumption of a well-sintered, high-quality solid electrolyte cathode with a typical interfacial area-specific resistance of approximately $50 \text{ ohm} - \text{cm}^2$, the estimated activation polarization voltage drops as a function of geometric current density at 25°C are given in Table 3.

Table 3: The activation polarization voltage drop, $|\eta_{act}^c|$, at 25°C :

$ i^c $ ($\text{mA} \cdot \text{cm}^{-2}$)	Estimated $ \eta_{S-act}^c $, (mV)	Operational significance
0.1	$\cong 5$	Typical low discharge rate, long-time cycling load
0.5	$\cong 25$	Standard moderate discharge rate
1.0	$\cong 50$	High-rate discharge/fast charge condition
2.0	$\cong 100$	High-rate discharge/fast charge condition

The activation polarization, $|\eta_{S-act}^c|$, at the cell cathode, $CoO_{2(s)}$, of typical thickness of $1 \mu\text{m}$ or less at temperatures $150, 200$, and 250°C as a function of the cell geometric current density, $|i^c|$, is given in the table 4 below.

Table 4: The activation polarization voltage drop, $|\eta_{S-act}^c|$ at the cell cathode, $CoO_{2(s)}$, as a function of the cell operating current density, $|i^c|$, and temperature:

Geometric $ i^c $ $\text{mA} \cdot \text{cm}^{-2}$	current density, $A \cdot \text{m}^{-2}$	$T = 150^\circ\text{C}$ $= 423.15K$ $ \eta_{S-act}^c $ (mV)	$T = 200^\circ\text{C}$ $= 473.15K$ $ \eta_{S-act}^c $ (mV)	$T = 250^\circ\text{C}$ $= 523.15K$ $ \eta_{S-act}^c $ (mV)
0.1	1	0.43	0.18	0.09
0.5	5	2.17	0.88	0.43
1.0	10	4.34	1.76	0.86
2.0	20	8.67	3.52	1.72

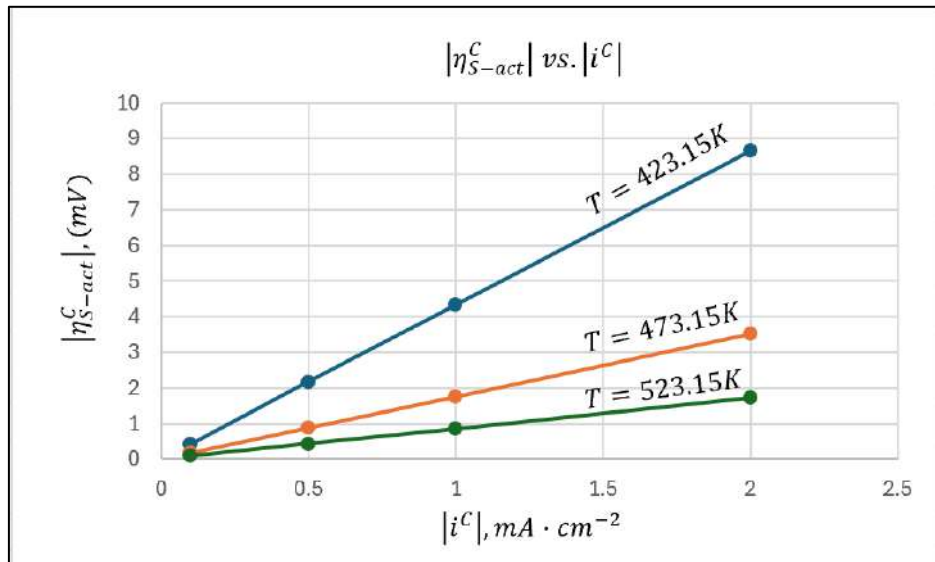


Figure 3: Activation polarization voltage drop at the cell cathode as a function of the geometric current density and temperature.

The cell anode activation polarization voltage drop, $η_{S-act}^A$ is given as a function of the cell operating current density, $|i^A|$ and temperature in Table 5 below.

Table 5: Activation polarization voltage drop at the cell anode, $LiC_6(s)$, of typical thickness of $1 \mu m$ or less, as a function of the geometric current density and temperature.

Geometric current density, $ i^A $		$T = 25^\circ C$ $= 298.15K$ $ η_{S-act}^A $ (mV)	$T = 150^\circ C$ $= 423.15K$ $ η_{S-act}^A $ (mV)	$T = 200^\circ C$ $= 473.15K$ $ η_{S-act}^A $ (mV)	$T = 250^\circ C$ $= 523.15K$ $ η_{S-act}^A $ (mV)
$mA \cdot cm^{-2}$	$A \cdot m^{-2}$				
0.1	1	8.49	0.12	0.04	0.02
0.5	5	37.65	0.62	0.22	0.09
1.0	10	66.51	1.23	0.43	0.19
2.0	20	98.55	2.46	0.86	0.37

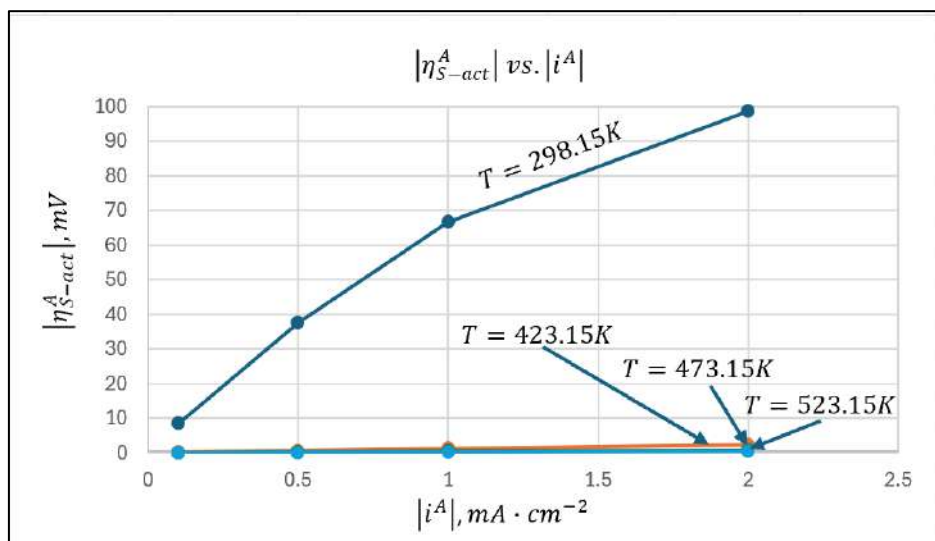


Figure 4: Activation polarization voltage drop at the cell anode as a function of the geometric current density and temperature.

From the data in Table 5, it is apparent that the activation polarization voltage drop at higher temperatures (150, 200 and 250°C) is negligibly small.

The specific lithium-ion diffusion-induced voltage drop in the cell anode, $\eta_{diffusion}^A$, during the cell discharge period is given in Table 6 below.

Table 6: The specific diffusion-induced voltage drop, $\eta_{diffusion}^A$, as a function of the geometric current density and temperature.

Geometric density, i_{geom} $mA \cdot cm^{-2}$	current $A \cdot m^{-2}$	$T = 25^\circ C$ $= 298.15K$ $\eta_{diffusion}^A (mV)$	$T = 150^\circ C$ $= 423.15K$ $\eta_{diffusion}^A (mV)$	$T = 200^\circ C$ $= 473.15K$ $\eta_{diffusion}^A (mV)$	$T = 250^\circ C$ $= 523.15K$ $\eta_{diffusion}^A (mV)$
0.1	1	3.41	0.06	0.02	0.01
0.5	5	17.05	0.30	0.11	0.05
1.0	10	34.09	0.61	0.22	0.10
2.0	20	68.19	1.22	0.44	0.19

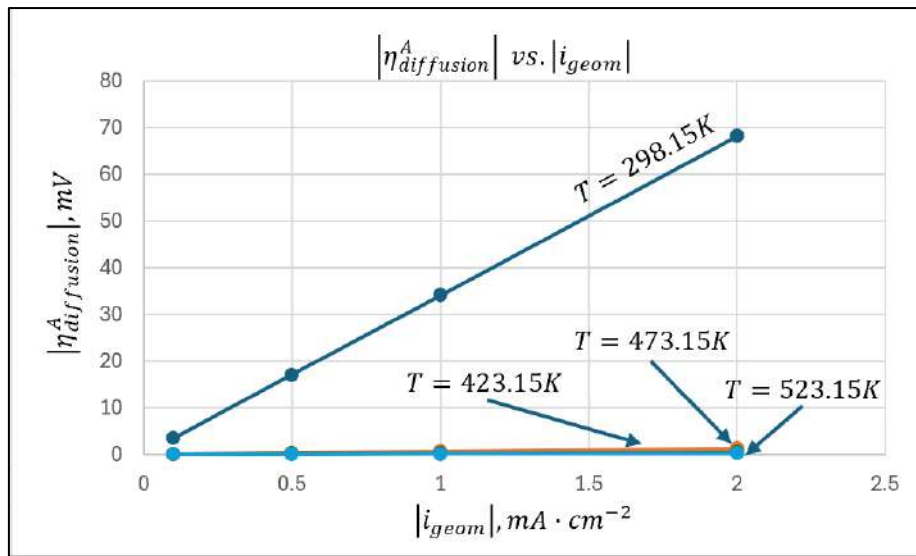


Figure 5: Diffusion-induced voltage drop, $\eta_{diffusion}^A$, as a function of the geometric current density and, temperature.

Notice that at higher temperatures, the diffusion induced polarization voltage drop in the cell anode $LiC_6(s)$ is negligibly small.

4. CONCLUDING REMARKS

The formulation provided in Section 2 was developed based on the principles of chemical engineering thermodynamics and electrochemical engineering. Then, the formulation was used to calculate the numerical data. The calculated data results for the electrochemical cell: $LiC_6(s)/Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}/CoO_2(s)$ are:

- The cell open-circuit voltage varies from 3.988 to 3.678 volt over the temperature variation from 25 to 250°C. The cell maximum electric efficiency varies from about 91 to 87% over the same temperature range. Also, the reversible thermal energy produced relative to the total thermal energy involved in the overall cell fraction varies from about 9.0 to 13.0% over the temperature from 25 to 250°C.
- For the cell electrolyte, $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98(s)}$, of $10\mu m$ thickness, the ohmic voltage drop varies from 5.0 to 0.10 mV for the cell temperature variation from 25 to 250°C at the geometric current density of $\left(\frac{1.0 mA}{cm^2}\right)$; whereas the ohmic voltage drop at the geometric current density of $\left(\frac{2.0 mA}{cm^2}\right)$ is from 10.0 to 0.2 mV for the same electrolyte thickness over the same temperature range. It is noted here that the delithiated cathode material $CoO_2(s)$ begins to decompose above 330 – 350°C. Also, $LiC_6(s)$ decomposes at 330°C.

- (c) For the cell electrolyte thickness of $20\mu m$, the ohmic voltage drop varies from 10.0 to 0.2 mV for the cell temperature variation from 25 to $250^\circ C$ at the geometric current density of $\frac{1.0 \text{ mA}}{cm^2}$; whereas at the geometric current density of $\frac{2.0 \text{ mA}}{cm^2}$, the ohmic voltage drop is from 20.0 to 0.4 mV for the same electrolyte thickness and the same temperature range.
- (d) At $25^\circ C$, the cell cathode activation polarization voltage loss is approximately 5, 25, 50 and 100 mV at the geometric current density of 0.1, 0.5, 1.0 and $2.0 \frac{mA}{cm^2}$, respectively.
For the same range of geometric current density, the cathode activation polarization voltage loss varies from 0.43 to 8.67 mV at $150^\circ C$; 0.18 to 3.52 mV at $200^\circ C$; and 0.09 to 1.72 mV at $250^\circ C$.
- (e) At $25^\circ C$, the cell anode activation polarization loss is approximately 8.5, 37.7, 66.5, and 98.60 mV respectively, at the cell geometric current density of 0.1, 0.5, 1.0 and $2.0 \frac{mA}{cm^2}$. Over the same range of the geometric current density, the anode activation polarization voltage loss varies from approx. 0.1 to 2.5 mV at $150^\circ C$; 0.0 to 0.9 mV at $200^\circ C$; and 0.0 to 0.4 mV at $250^\circ C$.
- (f) At $25^\circ C$, the cell anode specific diffusion-induced voltage loss is approx. 3.4, 17.1, 34.1, and 68.2 mV, respectively, at the cell geometric current density of 0.1, 0.5, 1.0, and $2.0 \frac{mA}{cm^2}$; whereas over the same range of geometric current density, the anode specific diffusion-induced voltage loss varies from approx. 0.1 to 1.2 mV at $150^\circ C$; 0.0 to 0.4 mV at $200^\circ C$; and 0.0 to 0.2 mV at $250^\circ C$.
- (g) At moderate current densities around $|i^c| = 1.0 \frac{mA}{cm^2}$, the lithium-ion concentration diffusion-related polarization voltage loss in the cell cathode varies from approx. 50 to 150 mV.
- (h) After accounting for the ohmic voltage loss in the cell electrolyte of thickness $10\mu m$, the activation polarization voltage losses in the cell anode and cathode electrodes, and the lithium-ion diffusion-specific voltage losses in the cell electrodes; the operational cell voltage for the geometric current density of $1.0 \frac{mA}{cm^2}$ was calculated at $250^\circ C$. Based on the operational cell voltage of 3.7820 volt and the cell open-circuit voltage of 3.7820 volt; the cell efficiency to convert the chemical energy into electrical energy was found to be about 95%.

Also, at $25^\circ C$ for the geometric current density of $1.0 \frac{mA}{cm^2}$, the computed electric power delivery is $(3.782 \times 10^{-3}) \frac{W}{cm^2}$.

Appendix:

(A-1) At $25^\circ C$, the base-line diffusion coefficient is, $D_{S,298} = 2 \times 10^{-14} \left(\frac{m^2}{s}\right)$; then, the diffusion coefficient, $D_{S,T}$, at another temperature, $T[K]$, can be obtained from:

$$D_{S,T} = D_{S,298} \exp \left[\frac{E_{a,d}}{k_B} \left(\frac{1}{298} - \frac{1}{T} \right) \right], \quad (53)$$

where $E_{a,d} = 0.35 \text{ eV}$ and $k_B = \text{Boltzmann constant} = 8.620 \times 10^{-5} \frac{\text{eV}}{K}$; and $\left(\frac{E_{a,d}}{k_B}\right) = 4060.3248 \text{ K}$

Typical lithium-ion concentration diffusion-related polarization voltage drops in the cell cathode of $CoO_2(s)$ at moderate current densities; e.g., around $|i^c| = 1 \text{ mA} \cdot \text{cm}^{-2}$ is between 0.05V and 0.15V (50 – 150 mV). Thin-design architectures feature exceptionally short diffusion lengths; however, the diffusion-related voltage drop scales non-linearly with the geometric current density at the cell cathode.

Example calculation for the determination of the actual cell voltage at $25^\circ C$ for the cell discharge current density of $1 \text{ mA} \cdot \text{cm}^{-2}$:

At $25^\circ C$ and $i_{geom} = 1 \text{ mA} \cdot \text{cm}^{-2}$, the total cell voltage loss is:

$$\begin{aligned} (\Delta V_{loss}^{tot}) &= \sum_{j=1}^{all} (\Delta V_{j,drop}) = [\Delta V_{electro}(t_S = 10\mu m)] + \eta_{act}^c + \eta_{act}^A + \eta_{diff}^c + \eta_{diff}^A \\ &= [(5) + (50) + (66.51) + (50) + (34.09)], (mV) \\ &= 205.60, (mV) = 0.2056 \text{ volt} \end{aligned} \quad (54)$$

$$\begin{aligned} \text{So, } V^{cell}(\text{at } 25^\circ C, i^{cell} = 1 \text{ mA} \cdot \text{cm}^{-2}) &= [U^\circ(\text{at } 25^\circ C)] - [\Delta V_{loss}^{tot}] = [3.9876 - 0.2056] \text{ volt} \\ &= 3.7820 \text{ volt} \end{aligned} \quad (55)$$

$$\begin{aligned} \text{Actual electric power delivery} &= V^{cell} \times i^{cell} = (3.7820 \text{ volt})(1 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}) \\ &= 3.7820 \times 10^{-3} \left(\frac{W}{cm^2}\right) = 3.782 \times 10^{-3} \frac{W}{cm^2} \end{aligned} \quad (56)$$

$$\text{Actual cell efficiency, } \eta_{actual} = \frac{V^{cell}}{U^\circ} = \left(\frac{3.7820 \text{ volt}}{3.9876 \text{ volt}}\right) = 0.9484 \cong 0.95 \equiv 95\% \quad (57)$$

(A-2) Relevant Thermodynamic data:

At $25^\circ C$:

$$\Delta H_{f,C_6(s)-graphite}^\circ = 0.0 \text{ kJ} \cdot \text{mol}^{-1}, \Delta G_{f,C_6(s)}^\circ = 0.0 \text{ kJ} \cdot \text{mol}^{-1}, S_{C_6(s)}^\circ = 5.77 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta H_{f,CoO_2(s)}^\circ = -240.2 \text{ kJ} \cdot \text{mol}^{-1}, \Delta G_{f,CoO_2(s)}^\circ = -217.6 \text{ kJ} \cdot \text{mol}^{-1}, S_{CoO_2(s)}^\circ = 40.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta H_{f,LiCoO_2(s)}^\circ = -678.2 \text{ kJ} \cdot \text{mol}^{-1}, \Delta G_{f,LiCoO_2(s)}^\circ = -615.1 \text{ kJ} \cdot \text{mol}^{-1}, S_{LiCoO_2(s)}^\circ = 52.6950 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta H_{f,LiC_6(s)}^\circ = -14.4 \text{ kJ} \cdot \text{mol}^{-1}, \Delta G_{f,LiC_6(s)}^\circ = -12.75 \text{ kJ} \cdot \text{mol}^{-1}, S_{LiC_6(s)}^\circ = 42.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Species heat capacity data:

$$C_{P,C_6(s)-graphite}^\circ = 6 \left(A + Bt + Ct^2 + Dt^3 + \frac{E}{t^2} \right), (J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}),$$

where

$$t = 10^{-3} T[K];$$

$$A = -2.035905, B = 7.356233, C = -2.3581428, D = 0.270790, E = 0.025444.$$

$$C_{P,CoO_2(s)}^\circ = \left(A + Bt + Ct^2 + Dt^3 + \frac{E}{t^2} \right), (J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}),$$

where

$$t = 10^{-3} T[K];$$

For $T = 400 - 700K$:

$$A = -40.71053, B = 6.411257, C = -6.010738, D = 4.150772, E = -0.007908.$$

For $T = 700 - 2700K$:

$$A = -47.17129, B = 14.679607, C = -3.696837, D = 0.794099, E = 0.330556.$$

$$C_{P,LiCoO_2(s)}^\circ = \left(A + Bt + Ct^2 + Dt^3 + \frac{E}{t^2} \right), (J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}),$$

where $t = 10^3 T[K]$;

For $T > 250K$,

$$C_{P,LiCoO_2(s)}^\circ = (A + Bt + Ct^2), (J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}),$$

where

$$T[K], A = 87.7 (J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}), B = 0.0214 (J \cdot \text{mol}^{-1} \cdot \text{K}^{-2}), C = (-1992000 J \cdot K \cdot \text{mol}^{-1})$$

[Ref. K. Chang, et.al. (ALPHA), 41(2013),pp.6-15]

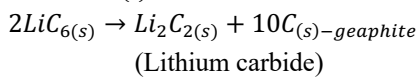
$$[C_p^\circ, LiC_6(s) \text{ at } 25^\circ\text{C}] \cong 74.3 \text{ to } 78.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

(depending on the carbon host density and its state of lithiation).

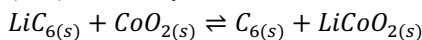
In battery design,

$$C_{p,LiC_6(s)}^\circ \cong C_{p,LiC_6(s),298}^\circ + k(T - 298.15), \text{ where } T[K].$$

Note: $LiC_6(s)$ decomposes at 330°C ($\cong 603.15K$);



(A-3) Thermodynamic data for the overall cell reaction:



$$\nu_{LiC_6(s)} = -1 \quad \nu_{CoO_2(s)} = -1 \quad \nu_{C_6(s)} = 1 \quad \nu_{LiCoO_2(s)} = 1.$$

or

$$\nu_1 = -1 \quad \nu_2 = -1 \quad \nu_3 = 1 \quad \nu_4 = 1.$$

The standard enthalpy change of the overall cell reaction at $T_0 = 298.15K$,

$$\Delta H_{T_0}^\circ = \sum_{j=1} \nu_j \Delta H_{f,j,T_0}^\circ = -423.6 \text{ KJ} \cdot \text{mol}^{-1} \text{ of the overall cell reaction.}$$

The standard Gibbs-free energy change of the overall cell reaction at

$$T_0 = 298.15K,$$

$$\Delta G_{T_0}^\circ = \sum_{j=1}^{j=4} (\nu_j \Delta G_{f,j}^\circ) = -384.75 \text{ kJ} \cdot \text{mol}^{-1} \text{ of the overall cell reaction.}$$

The standard entropy change of the overall cell reaction at $T_0 = 298.15K$,

$$\Delta S_{T_0}^\circ = \sum_{j=1}^{j=4} (\nu_j \cdot S_{j,T_0}^\circ) = -24.3050 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

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