Rechargeable magnesium cells are very promising candidates for future high energy density devices due to several advantages that are held by magnesium metal. In addition to its abundant availability (it is the eighth most abundant element), Mg possesses a moderate standard electrode potential (−2.356 V vs. SHE) albeit a very high volumetric density 3833 mAh/cm³ as well as a very high theoretical specific capacity of 2205 mAh/g. These factors make magnesium a promising candidate for high energy density cells.1,2,3 Magnesium-ion cells were initially studied for primary reserve battery technology using organic cathode materials by Gopukumar et al.4-11 to exploit high energy from multi-electron transfer reactions. Furthermore, unlike Li, Mg does not form dendrites, which could be a key factor in overcoming challenges like cell shorting and safety.12

However, Mg-ion cells must overcome the shortage of cathode materials by finding suitable materials which are compatible with the electrolytes and those that are able to host Mg²⁺ ions with high reversibility. Some of the Chevrel phase materials,13-18 and other cathode materials16-35 such as Mg iron silicates, vanadium oxides, molybdenum sulfides, borates and MnO₂ have been studied extensively with regard to their use as cathode materials for magnesium-ion cells. Some of the Mg²⁺ insertion mechanistic studies16-39 showed that most of these cathode materials possess very low solid-state Mg²⁺ ion diffusivity, which limits their high rate applicability. Moreover, Mg deposition from various electrolytes,40-44 including ionic liquids such as Mg chlorates, organic halides, organohaloaluminates, chloride-based electrolyte, inorganic nonaqueous electrolyte and polymer gel electrolytes,50-56 for solid-state Mg-ion cells has also been studied. It has been shown that Mg can behave with high reversibility only in solutions containing Grignard reagent dissolved in ether solvent such as tetrahydrofuran (THF) or Mg borohydride dissolved in dimethyl ether.57

Although there are multi-pronged studies undertaken to examine and characterize the electrode as well as the electrolyte materials for Mg-ion cells, there are no prior studies to model the insertion of Mg²⁺ into any of the electrodes. In the present study, an isothermal pseudo two-dimensional (P2D) porous electrode model35-38 was extended and modified to be used for the Mg-ion cell. A Bi electrode was used as an anode to be magnesiated and demagnesiated in the presence of 0.25 M C₂H₅MgCl-((C₂H₅)₂AlCl)₂ electrolyte. As mentioned in our previous work,62 a Bi electrode was chosen as an example of one of the alternative anodes, which can be used with conventional electrolytes avoiding the problem of the Mg²⁺ blocking layer at the Mg anode/conventional electrolyte interface. This was done to study the characteristics of Mg₂⁺ insertion reactions resulting from anode and electrolyte materials addressed toward the above-mentioned limitations. The study examined two different mechanisms: one based on direct 2-electron transfer and the other based on multi-electron transfer from each Mg atom in the Mg dimer present in the electrolyte. Electrochemical experiments were conducted to measure the electrochemical and transport properties of the Bi anode and electrolyte materials involved in the system.

Some of the parameters related to the electrolyte properties were measured and reported in our previous work.63 These parameters, along with the newly estimated parameters related to both the electrolyte and Bi electrode, were used as inputs in the modified anode half-cell model to predict the performance of the Bi anode electrode and also to understand the underlying phenomena and properties that dictate the characteristics of Bi electrode magnesiation and demagnesiation. In order for the porous electrode model to be used for conventional and other types of electrolytes with significant reversibility and coulombic efficiency, a proper description of electrolyte properties in terms of parameter values such as transference number, ionic conductivity as a function of electrolyte concentration, Mg salt diffusivity, and activity factor are essential in obtaining charge-discharge behavior of the cell. In this article, experimental methods for the measurement of parameters such as reaction rate constant on the Bi electrode, thermodynamic activity factor, Mg²⁺ solid-state diffusion coefficient, and porosity are described. The porous electrode model was employed to discuss the charge-discharge behavior of the Bi electrode at different rates, thermodynamic factors, Mg²⁺ solid-state diffusion coefficients, Bi electrode thicknesses and porosity.

**Experimental**

*Materials and coin cell fabrication.—* The electrolyte solution of 0.25 M EtMgCl-(Et₃AlCl) in tetrahydrofuran (THF) was prepared as reported previously62,63 based on the transmetallation reaction of magnesium chloride with ethylmagnesium chloride in tetrahydrofuran (THF) and a 0.01 M Mg salt solution was prepared by dissolving MgCl₂ in THF. Coin cells were fabricated in a dry box using 2032 coin cells. A 2 mm thick Bi electrode was used as an anode and a Mg foil ball was used as a counter electrode. The electrolyte solution was injected into a pyrex tube using a syringe and the tube was sealed using a PTFE stopper. A coin cell was assembled using the electrolyte-filled pyrex tube, an Li foil, and a tin foil. The coin cell was then sealed and allowed to stand for 24 hours before the electrochemical studies were initiated.

*Electrochemical experiments.—* Cyclic voltammetry was performed using a Princeton Applied Research model 273A potentiostat. All measurements were carried out at room temperature (25°C) with a scan rate of 10 mV/s. A 2 mm thick Bi electrode was used as an anode and a Mg foil ball was used as a counter electrode. The electrolyte solution was injected into a pyrex tube using a syringe and the tube was sealed using a PTFE stopper. A coin cell was assembled using the electrolyte-filled pyrex tube, an Li foil, and a tin foil. The coin cell was then sealed and allowed to stand for 24 hours before the electrochemical studies were initiated.

*Data analysis.—* The voltammetry data was fitted using the software OriginPro 8.5. The experimental data was fitted using a single exponential function. The fitted parameters were then used to calculate the faradaic efficiency of the Bi anode. The faradaic efficiency was calculated using the equation:

faradaic efficiency = \frac{C_{exp}}{C_{theo}}

where C_{exp} is the experimental charge and C_{theo} is the theoretical charge.
product of ethylmagnesium chloride (EtMgCl) Lewis base and diethylaluminum chloride (Et₂AlCl) Lewis acid in an inhibitor free THF solution with a 1:2 molar ratio of base to acid. The preparation of 0.25 M EtMgCl-(Et₂AlCl)₂ in THF and the following electrochemical measurements were carried out within a pure argon atmosphere in a M. Braun, Inc., glove box (< 1 ppm of water and oxygen).

The Bi electrode was prepared by first mixing 0.416 g of KF-polymer (12 wt% solution of PVDF in N-Methyl-2-pyrrolidone (NMP), Kureha) with 0.625 g of NMP (Sigma-Aldrich, anhydrous, ≥ 99.5%) followed by the addition of 100 mg of acetylene black (Denkikagaku Kogyo, HS-100, battery grade) powder in a sealed vial under constant stirring. After 20 minutes, 0.85 g of Bi (Sigma-Aldrich, purity, ≥ 99.99%, ~150 microns) powder was added to the vial and stirred for an additional 4 hours. The slurry was then coated on to copper (Cu) foil and dried overnight at 100 °C to evaporate NMP. Finally, electrodes with a diameter of 16 mm were punched and dried under vacuum (Precision vacuum oven model 19) at 120 °C for 18 hours at a pressure of ~30 inches Hg. Type 2032 coin cells were fabricated using the dried electrodes. Two sheets of Celgard 3501 surfactant-coated porous polypropylene were used as a separator (diameter: 19 mm), 0.25 M EtMgCl-(Et₂AlCl)₂ in THF was used as the electrolyte, and polished Mg metal foil (ESPI metals, 2N8, diameter: 16 mm) was used as the counter and reference electrodes. Two 0.5 mm thick stainless steel spacers, a spring, and a gasket were used in between the top and bottom stainless steel cans in the coin cell assembly. All cell fabrication was carried out within a pure argon atmosphere in a M. Braun, Inc., glove box (< 1 ppm of water and oxygen). Mg-ion cells were galvanostatically charged and discharged in an Arbin ABT 4.0 cycler.

Concentration cell.— In order to determine the activity factor of the electrolyte, the potential measurements of the electrolyte were performed on the Hitoff cell. Electrolyte preparation and the measurements were carried out within a pure argon atmosphere in a M. Braun, Inc., glove box (< 1 ppm of water and oxygen). A two-electrode cell was connected to an Autolab PGSTAT30 potentiostat (Brinkmann Instruments Co.). A platinum (Pt) electrode (2 mm) was used as working electrode and was placed in one side of the Hitoff cell. Magnesium ribbons (99.9% purity) were used as both the counter and reference electrodes, and were placed on the other side of the Hitoff cell. On the Pt electrode side, three different test electrolytes of concentrations 0.15 M, 0.2 M, and 0.25 M were placed, while a stock electrolyte of 0.3 M concentration was used as the reference electrolyte on the Mg electrode side. The two chambers were separated by a glass frit so that the solutions did not physically mix, but slow diffusion of solute was made possible through the glass frit over the course of measurement time. Steady-state potential measurements of the concentration cell were conducted for different test electrolyte concentrations using the potentiostat.

Cyclic voltammetry.— The reaction rate constant at the bis-muth/electrolyte interface, $k_0$, was estimated using cyclic voltammetry (CV). Electrolyte preparation and the following measurements were carried out within a pure argon atmosphere in a M. Braun, Inc., glove box (< 1 ppm of water and oxygen). The CV was conducted in a three-electrode cell with the Bi electrode coated on Pt (d = 2 mm) as a working electrode, the Mg ribbon (purity 99.9%) as the counter electrode and a Mg wire (purity 99.9%) as the reference electrode. The CV was performed under pseudo steady-state measurements of current by holding the cell at every 0.5 mV spacing for 10 s from OCV (0.35 V) to −0.1 V vs Mg/Mg²⁺. The current density of Mg insertion into Bi as a function of overpotential was recorded using the Autolab PGSTAT30 potentiostat (Brinkmann Instruments Co.).

Results and Discussion

Reaction rate constant.— The rate constant for Mg²⁺ insertion into the Bi electrode was calculated from the intercept of the tafel plot measured in a 3-electrode cell. For overpotentials less than 250 mV, the Tafel equation adequately describes the slow insertion of Mg²⁺ ions into Bi. Figure 1 shows the tafel plot obtained from the CV measurement. The intercept of the tafel equation is given by:

$$a = \frac{RT}{\alpha n F} \log i_0$$

where equilibrium exchange current density is defined as $i_0 = k_0 n F C_0$. In order to be used in the model as an input parameter, the reaction rate constant at the Bi/electrolyte interface was estimated through CV. The insertion of Mg²⁺ into the Bi electrode was observed at an overpotential onset of −0.18 V vs. Mg²⁺/Mg, in which the Mg₁Bi₂ alloy was formed through a 6 e⁻ transfer (2 e⁻ transferred per Mg atom resulting in 6 e⁻ transfer for 3 Mg atoms for the reaction stoichiometry as described in Equation 29). The figure also shows the Tafel plot within a potential window of −0.18 to −0.25 V vs. Mg²⁺/Mg. From the Tafel plot, the exchange current density ($i_0$) and the rate constant for Mg²⁺ insertion into the Bi electrode were found to be 1.08 mA cm⁻² and 7.47 × 10⁻⁶ m s⁻¹, respectively.

Thermodynamic activity factor.— The thermodynamic activity factor represents the potential losses which arise due to the change in concentration of the electrolyte. For typical Li-ion electrolytes, the activity factor is typically near zero, but it can be appreciably high at very large concentrations as well as at higher temperatures. Figure 2 shows...
the potential transients of the electrolyte for three different electrolyte concentrations in a concentration cell under zero applied current. The potential difference arises due to the concentration difference, and is related by Equation 2:

$$\nabla \varphi = \frac{v RT}{F} \left( 1 + \frac{d \ln f_z}{d \ln c} \right) \left( \frac{s_z}{n \nu_z} + \frac{\nu_0}{z_+ v_+} \right) \nabla \ln c$$  \[2\]

Using $v = 10$, $\nu_+ = 2$, $z_+ = 1$, $s_+ = -2$, and $n = 4$ based on the dimer $[\text{Mg}_2(\mu-\text{Cl})_6(\text{OC}_2\text{H}_5)_3]^+$ and other ions $\text{4-Ethyl-alumino-halo complexes}^-$, $2\text{Mg}^{2+}$, $3\text{Cl}^-$ and $\text{AlCl}^-\text{Cl}$ present in the electrolyte,65 the above equation can be rewritten as

$$\nabla \varphi = \frac{5 RT}{4F} \left( 1 + \frac{d \ln f_z}{d \ln c} \right) (1 - 2\nu_0) \nabla \ln c$$  \[3\]

From the above relation, the thermodynamic factor values were found to be 7.5 for 0.2 M and 21.3 for 0.25 M concentrations. Generally, for an electrolyte of dilute and higher concentrations, the mean molar activity coefficient is a strong function of electrolyte concentration and temperature. Concentration dependence of the mean molar activity coefficient arises due to the short-range ion-solvent interaction.66 For the Mg electrolyte under study, ion-ion interactions also might be occurring, and the ion-solvent interaction can be expected to be much higher due to the 1:2 ratio of a two-component solute system. According to a statistical-mechanical lattice theory,67 the non-electrostatic component of the activity coefficient can be estimated from the number of groups ($r = 11$) involved in an ionomer $\{[\text{Mg}_2(\mu-\text{Cl})_6(\text{OC}_2\text{H}_5)_3]^+\}$, the concentration of the individual solutes $([\text{C}_2\text{H}_5\text{MgCl}](\text{C}_2\text{H}_5)\text{AlCl}_3)\text{B}$ ($N_r$), and the solvent ($N_s = 12.3$) for a liter volume of solvent (THF). The non-electrostatic component of the activity coefficient, representing the non-ion-solvent interaction, is given by,

$$\ln f = \ln \left( \frac{N_r + N_s}{r N_r + N_s} \right) + (r - 1) \frac{(r N_r)}{(r N_r + N_s)}$$  \[4\]

Table I. Comparison of thermodynamic activity factor estimated from the experiment and theoretical estimation of non-electrostatic component of the mean molar activity coefficient of $\text{C}_2\text{H}_5\text{MgCl}-2(\text{C}_2\text{H}_5)\text{AlCl}$ electrolyte.

| Concentration (M) | Cell Potential, $\psi$ (V) | $\Delta \psi$ (V) | $\Delta f_{\pm}$ at $c$ (expt) | $N_r$ | $\Delta f_{\pm}$ at $c$ (theory) | $d \ln f_{\pm}/d \ln c$ | $d \ln f_{\pm}/d \ln c$ (theory) |
|------------------|--------------------------|-----------------|-------------------------------|-------|-------------------------------|--------------------------|-----------------------------|
| 0.15             | 1.53                     | 0.07            | 21.3                          | 0.45  | 0.75                          | 12.6                     | 12.6                        |
| 0.2              | 1.60                     | 0.07            | 21.3                          | 0.60  | 6.2                           |                          | 6.2                         |
| 0.25             | 1.74                     | 0.14            | 21.3                          | 0.75  | 12.6                          |                          | 12.6                        |

Table II. $\text{Mg}^{2+}$ solid-state diffusion coefficient results estimated from GITT method.

| Method | Unit   | 20% SOC | 20% DOD | 40% DOD | 60% DOD |
|--------|--------|---------|---------|---------|---------|
| D, GITT | $m^2.s^{-1}$ | $1.31 \times 10^{-17}$ | $2.40 \times 10^{-17}$ | $4.82 \times 10^{-17}$ | $1.99 \times 10^{-18}$ |

which can be truncated to the form,

$$\ln f \sim \left( \frac{r - 1}{r N_r + N_s} \right)^2$$  \[5\]

Table I shows the comparison of thermodynamic factors calculated from the experiments and the lattice theory. At 0.2 M concentration, the calculated values were found to be similar to the theoretical values. However, at 0.25 M concentration, the theoretical values were found to be lower than the experimental values. The difference is possibly due to an electrostatic ion-ion interaction, which is ascribed to be smaller for lower concentrations but can be significantly larger for higher concentrations.

$\text{Mg}^{2+}$ solid-state diffusion coefficient.—The solid-state diffusion coefficient was measured by the galvanostatic intermittent titration technique (GITT) method68 in a two-electrode 2032 coin cell geometry. Open circuit voltage relaxation ($\delta E/\delta t^{1/2}$) was measured from the cell voltage transients in GITT method during application of a 30 s discharge/charge pulse at selected states of charge and depths of discharge. A sample GITT pulse profile and the corresponding cell voltage transient is shown in Figure 3. $\delta E/\delta t^{1/2}$ was calculated from a Mg-Bi coin cell. The solid-state diffusion coefficient was calculated from Wepchner-Huggins equation:69

$$D_{\text{Mg}^{2+}} = \frac{4}{\pi} \left[ \left( \frac{V_s}{\text{SF}} \right) \left( \frac{\delta E}{\delta t^{1/2}} \right) \right]$$  \[6\]

The BET area found from the experimental data fit is 0.7 m$^2$. g$^{-1}$. The molar volume of bismuth “$V_m^{\text{Bi}}$” is 160.85 cm$^3$. mol$^{-1}$, and the $\delta E/\delta t^{1/2}$ was found to be 0.102293. The slope $\delta E/\delta t^{1/2}$ was estimated from the cell voltage transients resulting from the applied GITT pulse. The cell voltage transients at selected states of charge and discharge are shown in Figure 4 as a plot of $E$ vs. $t^{1/2}$. The diffusion coefficient results are tabulated in Table II.

$\text{Electrode porosity}$.—Electrode porosity and the volume fraction of each component in bismuth (9.78 g. cm$^{-3}$), carbon (0.4 g. cm$^{-3}$) and binder (1.77 g. cm$^{-3}$) electrode matrix were calculated from particle density information. As the loading level of each component is known, the expected volume occupancy can be estimated under tapped filling in a cylinder of known dimensions. For an 80-10-10 mixture of Bi-C-PVDF, the void volume, volume fraction of Bi, and electrolyte is

![Figure 3. Galvanostatic Intermittent Titration Technique (GITT) pulse schedule and the voltage transients during the applied current pulse.](image)
calculated from the equation given by the following Equations 7a–7c:

\[ V_{\text{void}} = V_c - \left( \frac{w_{\text{Bi}}}{\rho_{\text{Bi}}} + \frac{w_{\text{carbon}}}{\rho_{\text{carbon}}} + \frac{w_{\text{PVDF}}}{\rho_{\text{PVDF}}} \right) \]  

\[ \varepsilon_{\text{Bi}} = \frac{w_{\text{Bi}}}{\rho_{\text{Bi}}} \]  

\[ \varepsilon_{\text{electrolyte}} = \frac{V_{\text{void}}}{V_c} \] 

The calculated volume fraction values for 70% compression were found to be 0.079 for Bi, 0.623 for electrolyte, and 0.298 for carbon and binder put together. Hence, very high density of Bi enables the electrode to be designed with high electrode porosity. A summary of parameters describing kinetic and transport properties of solid-phase Bi and Mg electrodes and Mg electrolyte is listed in Table III.

**Model Schematics**

A schematic of the Bi/electrolyte/Mg anode half-cell (Bi-Mg) is described in Figure 5, where the pseudo two-dimensional (P2D) electrochemical model takes into account the reversible solid insertion/extraction of Mg\(^{2+}\) as well as porosity effects will be neglected in a solid Mg electrode. Generally, a Mg-ion cell consists of the current collector, the positive electrode, the separator, and the negative electrode. A Magnesium organohaloaluminate solution fills the porous components and serves as the electrolyte. The governing equations of the model are listed in Table IV. Solid phase equations are discretized along a dimensionless radii, \(y = r/r_p\). In all the governing equations, the subscript \(i = p\) denotes the positive electrode, \(i = s\) denotes the separator and \(i = n\) denotes the negative electrode.

Transfer coefficients are assumed to be equal to 0.5 and \(i_0\) is the equilibrium exchange current density. \(\alpha\)-Mg\(_3\)Bi\(_2\) electrode reference potential, \(E_{\text{ref}}(\text{SOC})\), is defined from the average of \(\alpha\)-Mg\(_3\)Bi\(_2\)/Mg (Bi-Mg) half-cell C/50 rate charge discharge data as shown in Figure 6. \(c_{i,\max,p}\), maximum concentration of Mg\(^{2+}\) in Bi electrode was calculated to be 84,400 mol. m\(^{-3}\) based on the 10.86 mg loading of Bi with 3/2 atoms of Mg inserted per Bi atom into the positive electrode.

A cell sandwich model of Bi-Mg cell with 0.25M C\(_2\)H\(_5\)MgCl-(C\(_2\)H\(_5\))\(_2\)AlCl\(_2\) electrolyte, as shown in Figure 5, was built with the parameters listed in Table III and functions corresponding to \(\alpha\)-Mg\(_3\)Bi\(_2\) and Mg electrode potentials. The partial differential equations (equations 8–28 listed in Table IV) were solved in a COMSOL multiphysics.
Table IV. List of Governing Equations.

| Eqn. # | Equations | Description |
|--------|------------|-------------|
| 8      | $y^2 \left( \frac{\partial y}{\partial x} \right) + \left( \frac{y^2}{D_{ij}} \frac{\partial \psi}{\partial x} \right) + \frac{\gamma_{ijl}}{\gamma_{ijl}(1 - \gamma_{ijl})} = 0$ | Fick’s II law in spherical particle for solid phase Mg material balance |
| 9      | $D_{ij} \frac{\partial \psi}{\partial x} = 0$ | No flux condition at the centre of the particle |
| 10     | $D_{ij} \frac{\partial \psi}{\partial x} = \frac{\rho_{ij}}{ho_{ij}(1 - \gamma_{ijl})}$ | Rate of Mg-ion flux transfer across the electrode surface/electrolyte interface |
| 11     | $L_i \frac{\partial \phi}{\partial r} = \nabla \cdot \left( \frac{D_{ij} \nabla \phi}{\partial r} \right) + \frac{L_i \sigma_{ijl}}{\partial r} \left( 1 - 2 \phi \right)$ | Mg-ion material balance in the liquid-phase binary electrolyte |
| 12     | $D_{ij} \frac{\partial \phi}{\partial r} = 0$ | No mass flux condition at two current collector ends $x = 0$ and $x = L$ |
| 13     | $D_{ij} \frac{\partial \phi}{\partial r} = D_{ij} \phi_{B^+}$ | Effective Mg-ion diffusion coefficient in the liquid-phase binary electrolyte |
| 14     | $L_i \nabla \phi = \nabla \cdot \left( \frac{D_{ij} \nabla \phi}{\partial r} \right) = -L_i S_{ijl} \phi_{loc,l,i}$ | Ohm’s Law for solid-phase charge balance |
| 15     | $\phi_{eff,l,i} = \kappa_{ijl} \phi \left( 1 - \frac{e_i e_f}{\epsilon} \right)$ | Effective electrical conductivity of positive and negative electrodes |
| 16     | $S_{ijl} = \left( \frac{\rho_p}{\rho_p} \right) \left( 1 - \frac{e_i e_f}{\epsilon} \right)$ | Specific surface area per unit volume of the positive and negative electrodes |
| 17     | $\kappa_{ijl} \frac{\partial \phi_{loc,l,i}}{\partial x} = \frac{f_{app}}{L}$ | Charge flux at the current collector - positive electrode interface |
| 18     | $\kappa_{ijl} \frac{\partial \phi_{loc,l,i}}{\partial x} = \frac{f_{app}}{L}$ | Charge flux at the separator - positive electrode interface |
| 19     | $\kappa_{ijl} \frac{\partial \phi_{loc,l,i}}{\partial x} = 0$ | Charge flux at the separator - negative electrode interface |
| 20     | $\kappa_{ijl} \frac{\partial \phi_{loc,l,i}}{\partial x} = 0$ | Solid-phase potential boundary conditions |
| 21     | $\nabla \cdot \left( \frac{D_{ij} \nabla \phi}{\partial r} \right) = \frac{4 \pi \rho_i}{m} \left( 1 - \frac{e_i e_f}{\epsilon} \right) \left( 1 - 2 \phi \right) \frac{1}{\partial r} \left( 1 - 2 \phi \right) \nabla$ | Ohm’s law for charge balance in binary electrolyte |
| 22     | $\kappa_{ijl} = \kappa_{ijl}(R_B^{eff})$ | Effective diffusion coefficient in the binary electrolyte |
| 23     | $\kappa_{ijl} = -7.872c_l^2 + 6.063c_l - 9.13$ | Ionic conductivity as a function of electrolyte concentration \(^{263}\) |
| 24     | $\kappa_{ijl} = \kappa_{ijl}(R_B^{eff})$ | No charge flux condition at positive electrode current collector boundary |
| 25     | $\kappa_{ijl} = \kappa_{ijl}(R_B^{eff})$ | No charge flux condition at negative electrode current collector boundary |
| 26a    | $j_{loc,l,i} = i_{0,loc} \left( \frac{2a_i F \nu_i}{R_B^{eff}} \right) \exp \left( \frac{-2a_i F \nu_i}{R_B^{eff}} \right)$ | Butler-Volmer formulation for Mg-ion flux transfer across the interface through direct 2e\(^{-}\) mechanism |
| 26b    | $j_{loc,l,i} = i_{0,loc} \left( \frac{2a_i F \nu_i}{R_B^{eff}} \right) \exp \left( \frac{-2a_i F \nu_i}{R_B^{eff}} \right)$ | Butler-Volmer formulation for Mg-ion flux transfer across the interface through multi-e\(^{-}\) mechanism |
| 27     | $\eta_i = \phi_{loc,l,i} - \phi_{c,1} - E_{ref(c,1,surf,j)}$ | Overpotential as function of solid-phase and liquid-phase potentials |
| 28a    | $\eta_i = F k_{B} c_{i(1,\text{max},i)} - c_{1,\text{surf},j}^{0.5} - c_{1,\text{surf},j}^{0.5}$ | Exchange current density for direct 2e\(^{-}\) mechanism |
| 28b    | $\eta_i = 2 F k_{B} c_{i(1,\text{max},i)}^{0.5} - c_{1,\text{surf},j}^{0.5} - c_{1,\text{surf},j}^{0.5}$ | Exchange current density for multi-e\(^{-}\) mechanism |
| 29     | $3 \text{Mg} + 2 \text{Bi} \leftrightarrow \alpha - \text{Mg}_2\text{Bi}_2, \quad E_0 = 0.279 \text{ V} \text{ vs. Mg/Mg}^{2+}$ | Magnesium insertion reaction |

3.5a software package. One-dimensional (1-D) meshing was configured with 36 mesh points, 35 mesh elements, and 4 boundary elements in the length scale. The variables solved in 1-D scale are Mg salt concentration ($c_l$), solid-phase potential ($\psi$), liquid-phase potential ($\psi_2$), and pore-wall flux ($j_{loc}$). Two-dimensional (2-D) meshing was configured with 109 mesh points, 166 triangular mesh elements, 48 boundary elements, and 8 vertex elements. In 2-D scale, only solid-phase Mg concentration ($c_l$) is solved along both length and radial directions. Model equations were discretized in time by a Backward Differentiation Formula of order ranging between 1 and 3. Time discretization was configured with a maximum time step of 5 s for 0.05 C-rate, and 2 s for 0.25 C-rate and 1C-rate models. The compiled equations were solved in a Direct UMFPACK linear system solver.

Results and Discussion

The theoretical capacity of the Bi electrode is reported as 0.386 Ah.g\(^{-1}\).\(^{71}\) From the BET area of 0.7 m\(^2\).g\(^{-1}\) obtained from the model fit with the experimental data, the calculated area-specific capacity was found to be 0.55 Ah. m\(^{-2}\). The Bi electrode undergoes pulverization during magnesiation due to reaction 29, to form $\alpha$-Mg$_2$Bi$_2$. In our previous work,\(^{62}\) the average particle size of pristine Bi was found to vary between 60 to 150 microns, which during repeated cycling at 0.1 C-rate undergoes pulverization and reduces to 5 - 10 nm nanocomposite particles after complete demagnesiation. The extent of pulverization is expected to be dependent on the rate of charge and discharge. Hence, a correction factor for the BET area was applied based on the model fit with the experimental data. Although the active surface changes during the charge/discharge, the mass of the active material is expected to remain the same. For the multi-electron mechanism as shown in Equation 26b, an apparent current density was deduced by applying a correction factor of 11.8 for a C/20 rate, 6.1 for a C/4 rate and 3.1 for a 1 C rate respectively to the BET surface area. These correction factors indicate that bismuth undergoes severe pulverization at higher charge rates and hence starting with a small particle size pristine Bi will be the key for improving higher C-rate performance. For the direct 2-electron transfer mechanism as shown in Equation 26a, an apparent current density was deduced by applying a correction factor of 8.1 for a C/20 rate, 6.1 for a C/4 rate and 5.2 for a 1 C rate respectively to the BET surface area. Electrochemical
Figure 7. Charge-discharge rate effects on electrolyte concentration distribution with multi-electron mechanism at 100% SOC and 100% DOD during discharge of Bi-Mg cell.

Figure 8. Charge-discharge rate effects on modeled cell voltage-capacity profile of Bi-Mg cell with multi-electron transfer mechanism (solid/dashed lines: experiment; symbols: model).

Figure 9. Charge-discharge rate effects on modeled cell voltage-capacity profile of Bi-Mg cell with direct 2-electron transfer mechanism (solid/dashed lines: experiment; symbols: model).

modeling of Bi-Mg cell with 0.25M C2H5MgCl−([C2H5]2AlCl)2 was performed on a 1.54 cm2 cell size with an applied current of 0.1705 A. m−2 for a 1 C-rate discharge (Mg2+ insertion into Bi). The capacity obtained from the model is presented in this article with a correction factor of 92.75% (accounting for the deviation in capacity predicted by the model at 0.1C discharge rate) to the modeled capacity to fit with the experimental data. To predict the factors governing the electrochemical performance of Mg2+ insertion/extraction into Bi electrode, this study examined the effects of thermodynamic factors, the Bi electrode thickness and porosity, the solid-state diffusion, and the charge/discharge rate on Mg electrolyte concentration across the thickness of the cell and cell voltages. Furthermore, the estimated parameters representing the fundamental electrode and electrolyte properties as well as the cell and electrode geometry of the coin cell experimental studies for electrochemical performance in terms of cell thickness, particle size, cross-sectional area, and active material loading were studied. All the c2 comparisons are being performed at end of charge and discharge status of the cell. As indicated in the model schematics, co-ordinate 2 represents the boundary near the separator and co-ordinate 3 represents the boundary near the current collector in all of the following results when it is not mentioned.

C-rate effects.—Figure 7 shows the modeled Mg electrolyte concentration distribution with multi-electron transfer mechanism at 100% SOC and 100% DOD for the Bi-Mg cell for the Bi electrode with 60 μm thickness, TDF = 20, and 0.623 porosity at three discharge rates of 0.05, 0.25, and a 1 C-rate. At 100% SOC, the electrolyte concentration remains uniform across the electrode for all charge rates, but the electrolyte concentration level tends to decrease with increasing charging rates. Uniform distribution of electrolyte concentration during charge is possibly attributed to the large surface area generated due to the pulverization of the Bi electrode (small particle size) that occur during the course of the magnesiation. It can be inferred that for low discharge rates (0.05 and 0.25 C-rate) the electrolyte concentration at the end of discharge tends to be more even across the electrode thickness and the values were also not very high from the initial electrolyte concentration (<275 mol/m3). However, at higher discharge rates (>0.25 C) the Bi electrode accumulates more electrolyte (>300 mol/m3). Additionally, at these conditions, gradients in the rate of reaction at the electrode/electrolyte interface grow, especially in 40% of the electrode thickness near the current collector boundary region. This becomes a major limiting factor in de-magnesiation from the α-Mg2Bi3, which affects the cell’s performance. Due to the very small Bi particle size around 0.1 nm and better diffusion rate values, the electrolyte concentration did not fall as low as 0.15 M during the course of entire charge and discharge—where the equilibrium of the electrolyte undergoes major shift to associate themselves rather than dissociate readily in the charged electrolyte. Modeled cell voltages with the multi-electron transfer mechanism indicate a polarization loss of 110 mV at 50% DOD/SOC from discharge/charge at 0.05 C-rate to 1 C-rate, which was found to be 30 mV more than the model estimates with large Bi particle and higher diffusion rates. Modeled cell voltages with the multi-electron transfer mechanism shown in Figure 8 were found to fit better at lower (0.05 and 0.25 C-rate) charge/discharge rates with the experimental coin cell performance, but at a 1 C-rate, the model fails to fit with the experimental cell performance. The large difference between the model and experiment at a 1 C-rate is attributed to the large variation in diffusivity because of large gradients in electrolyte concentration. Modeled cell voltages with the direct 2-electron transfer mechanism shown in Figure 9 were found to fit lesser at lower (0.05 and 0.25 C-rate) charge/discharge rates with the experimental coin cell performance. However, at a 1 C-rate, the model shows very large overpotential and thus fails to completely fit with the experimental cell performance. Therefore, in the remainder of this article, all discussions on the results will be based on the multi-electron mechanism only.
Thermodynamic factor effects.—Figure 10 shows the Mg electrolyte concentration variation for the Bi-Mg cell at 0.25 C-rate for four different thermodynamic factors (TDF): $d \ln f_\parallel / d \ln c$ of 0, 10, 20, and 54 at 100% SOC and 100% DOD. It can be inferred that for the TDF in the entire range of 0 to 54, the electrolyte concentration at 100% SOC tends to be similar, and the gradients across the entire electrode thickness range were not present due to the large surface area created by pulverization. At 100% DOD, the gradients in $c_2$ across the electrode increase for TDF between 0 and 10. For a TDF range between 20 and 54, the electrolyte concentration gradients remain similar for the 50% of the electrode thickness. However, the gradients in $c_2$ tend to decrease and the $c_2$ distribution becomes uniform across the other half of the electrode thickness. This is because of the absence of concentration gradients arising due to the large potential loss and decreased activity of the electrode region near the current collector.

Figure 11 shows the cell voltages for the Bi-Mg cell at 0.25 C-rate for the four different thermodynamic factors (TDF) of 0, 10, 20, and 54. The difference in the charge and discharge potentials was found to grow with the increase in TDF values even at low 0.25 C-rate of discharge. Hence, it is most important to choose an electrolyte with the least thermodynamic factor to minimize the thermodynamic penalty that arises due to the electrolyte activity. For example, electrolytes with concentrations from 1 to 4 M LiPF$_6$ have been reported$^{65,73}$ to have thermodynamic factor of less than 4 at room temperature. In Li-ion chemistry, the difference in the charge and discharge potentials is found to stem only from cell resistances and the electrolyte is said to have the smallest role in the electrode performance.

Mg$^{2+}$ solid-state diffusion effects.—Figure 12 shows the electrolyte concentration distribution at 100% SOC and 100% DOD, and cell voltages during 0.25 C-rate discharge of Bi-Mg cell.
cell voltages for the Bi-Mg cell at a 0.25 C-rate for three different solid state Mg$_{2+}$ diffusion coefficients (at 0.623 porosity) of $1 \times 10^{-12}$, $1 \times 10^{-14}$, and $1 \times 10^{-17}$ m$^2$.s$^{-1}$. As observed in previous cases, the electrolyte concentration distribution across the electrode remained uniform for all diffusivity values after complete charging. Similar uniform concentration distribution is observed after complete discharge for diffusivities $1 \times 10^{-14}$ m$^2$.s$^{-1}$ and higher. It can be observed that for a diffusion rate of $10^{-17}$ m$^2$.s$^{-1}$ the electrolyte concentration across the cell thickness at 100% DOD begins to develop large gradients of more than 20 mol/m$^3$ at a slow 0.25 C-rate of discharge. A diffusion limitation begins to set in for the electrode region toward the separator interface for a diffusion rate at $10^{-17}$ m$^2$.s$^{-1}$. The reaction rate begins to slow down as the electrode/separator interface is approached. Such diffusion limitation is absent for diffusion rates of $10^{-14}$ m$^2$.s$^{-1}$ and above. These results suggest that a small Bi particle size is required to counter the limitations offered by slow diffusion even at slow discharge rates. Cell voltages for all diffusion rates ranging between $10^{-12}$ m$^2$.s$^{-1}$ and $10^{-17}$ m$^2$.s$^{-1}$ do not show significant variation at a slow 0.25 C-rate of discharge but do show a 3% improved discharge capacity at higher diffusion rates above $10^{-14}$ m$^2$.s$^{-1}$.

**Electrode porosity effects.**—Figure 13 shows the Mg electrolyte concentration distribution at 100% SOC and 100% DOD as well as cell voltages for the Bi-Mg cell at a 0.25 C-rate for four different Bi electrode (60 μm thick) porosities of 0.3, 0.444, 0.55, and 0.623. It can be inferred that for increasing electrode porosities the electrolyte concentration gradients become more uniform across the electrode thickness. The nearly linear gradients was observed for the 0.623 Bi electrode porosity, which indicates the even distribution of pore wall flux rates (Mg$^{2+}$ insertion reaction rate) across the cell’s thickness. However at lower porosities of 0.55 and below, the gradients were found to be larger. This was mainly due to a lesser penetration of the electrolyte into half of the thickness of the Bi electrode toward the current collector boundary. Thus, at porosities of 0.55 and below 50% of cell thickness (~30 μm) is rendered an ineffective zone even at a low 0.25 C-rate of discharge, which is attributed to be an implication of low electrolyte diffusion rates. However, the effect of vast changes in electrode porosities on cell voltages at a low 0.25 C-rate of charge and discharge remains meager with the exception for the minimal difference in discharge capacity between all the electrode porosities.

**Electrode thickness effects.**—Figure 14 shows the Mg electrolyte concentration distribution at 100% SOC and 100% DOD as well as cell voltages for the Bi-Mg cell for four different Bi electrode (0.623 porosity) thicknesses of 80, 60, 40, and 25 μm. It can be inferred that for an electrode that is 25 μm thin the electrolyte concentration gradients across the electrode were less than $\pm 10$ mol. m$^{-3}$ at both 100% SOC and 100% DOD. As the pore wall flux rates across the cell thickness is expected to be uniform for a lower thickness, smaller accumulation in the separator phase was observed. This suggests the possibility of uniform reaction rates from near the separator region. As the thickness of the Bi electrode is increased to 40 μm and 60 μm, the gradients were found to steadily grow even larger and the gradients were as high as $\pm 30$ mol. m$^{-3}$ for 80 μm electrode. As the thickness of the electrode increases, the limitations of the electrolyte diffusivity becomes apparent, which results in large concentration gradients and subsequently limits the availability of the electrolyte at the various reaction zones. Cell voltages for an electrode of 25 to 80 μm thickness were found to gradually vary, with overpotentials that increased with cell thickness. A thicker electrode causes severe potential loss and at the same time contributes to discharge capacity loss of 10% even at a 0.25 C-rate of charge and discharge. This is due to the proportionally decreasing mass loading of Bi at a lower thickness and discharge at higher nominal discharge rates. Thus, these results suggest electrodes that are too thin provide uniform electrolyte concentration gradients and minimize energy loss, but they have limited space to pack sufficient active material. In contrast, the cells with greater thicknesses allow for larger energy loss and a large part of the electrode remains unutilized as well. Hence 40 μm proves to be an attractive candidate in comparison to both the thin and thicker electrodes, which increases the possibility of higher reaction rates throughout the cell’s thickness.

The P2D model also predicted the solid phase Mg concentration across the cell at all radii of the particle. Since a very small (0.1 nm) particle size was employed in the model, the solid phase Mg concentration varied little in space. Yet, the variation of Mg solid phase concentration was evident throughout the charge and discharge time period. Figure 15 depicts the amount of Mg magnesiated into Bi at various charge and discharge rates with a multi-electron transfer mechanism. It is evident from this figure that very low solid phase Mg diffusivity has its toll on the faster discharge rates. At faster rates, the amount of Mg magnesiated is less than 50% and hence the discharge capacity is reduced significantly. Overall, the modeling results—which account for parameters corresponding to the properties of the actual materials and the actual cell geometry—suggest that electrodes with a diffusion coefficient higher than $10^{-14}$ m$^2$.s$^{-1}$, an electrolyte with a lower thermodynamic factor (preferably less than 5), better inherent system properties such as a transfer number (>0.2), and salt diffusion coefficients higher than $10^{-11}$ m$^2$.s$^{-1}$ are critical to improve the high-rate performance of Bi-Mg cells.

Model results at different C-rates were compared with experimental coin cell data in Figures 8 and 9. They were found to fit very closely with the experimental results at low rates of charge and discharge. Nevertheless, at higher rates the model results did not show high accuracy fit with the experimental data due to the large gradients in electrolyte concentration. The following assumptions were major drawbacks in the model: (a) a uniform diffusion co-efficient and transfer number at all states of charge and discharge, (b) the absence of systematic and dynamic equations to track the changes in particle size and active surface area at all states of charge and discharge, (c) the absence of constitutive equations describing the potential and stress coupling that will be predominant during the pulverization of Bi electrode, (d) the absence of phase-field equations describing phase separation occurring during magnesiation, and (e) the low electrode porosities were assumed in solid Mg electrode to account for the
approximated situation of moving Mg/electrolyte boundaries during Mg deposition and dissolution.

Conclusions

Transport and electrochemical properties of Mg$^{2+}$ ions in a magnesium organohaloaluminate electrolyte estimated from experiments were used as parameter inputs to the pseudo two-dimensional model to describe the electrode reactions occurring at a Bi electrode. Two different models with direct 2-electron transfer mechanism and multi-electron transfer mechanism were studied, and the multi-electron transfer mechanism was found to agree closely with the experimental data. A very low transference number value causes the Mg$^{2+}$ ion to rely more on diffusivity rather than on migration during magnesiation/demagnesiation. This results in a large concentration gradient across the electrode and consequently significant voltage loss. The percolation threshold for the solid state Mg$^{2+}$ diffusion coefficient was found to be $10^{-14}$ m$^2$.s$^{-1}$ above which the cell performance could be improved. At very low diffusion rates below $10^{-14}$ m$^2$.s$^{-1}$, the diffusion effects remarkably lowered the reaction rate at the local electrode/electrolyte interfaces by an order of magnitude rendering a large part of the Bi electrode inactive. Solid-phase Mg concentration across the electrode’s thickness and particle radius during magnesiation and de-magnesiation suggested the lack of complete magnesiation at faster charge rates, which resulted in significant capacity loss. Also, a 40 μm thick Bi electrode was found to be optimum as it could pack a significant amount of active material. Some of the modeling and other experimental studies showed that when electrolyte concentrations fell below 0.15 M, the electrolyte loses its stability and efficiency, which dramatically affects the electrode and cell performance. These results indicate the underlying reason for the failure of Bi-Mg cells at discharges rates near and greater than 1 C. Modeled cell voltages indicate a polarization loss of 110 mV at 50% DOD from discharge at rates of 0.25 C to 1 C. Electrodes with diffusion coefficients higher than $10^{-14}$ m$^2$.s$^{-1}$, should utilize an electrolyte with a lower thermodynamic factor (preferably less than 5), and better inherent system properties such as transference number (>0.2), which are necessary to improve the high-rate performance of Bi-Mg cells.

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### List of Symbols

- **a** Tafel intercept
- **Br_i** Bruggeman coefficient \((i = p, i = s\) and \(i = n\) in positive and negative electrode and separator
- **c** Test electrolyte salt concentration in concentration cell
- **C_i** Bulk Mg electrolyte concentration in test experiment
- **c_{i,i}** Mg-ion concentration \((i = p\) and \(i = n\) in positive and negative electrode active material
- **c_{2,i}** Electrolyte salt concentration \((i = p, i = s\) and \(i = n\) in positive and negative electrode and separator
- **c_{1.max,i}** Maximum Mg-ion concentration \((i = p\) and \(i = n\) in positive and negative electrode active material
- **c_{1.surf,i}** Mg-ion concentration \((i = p\) and \(i = n\) in positive and negative electrode active material surface
- **D** Salt diffusion coefficient in electrolyte
- **D_{1,i}** Mg-ion diffusion coefficient \((i = p\) and \(i = n\) in positive and negative electrode active material
- **D_{2,i}** Liquid phase Mg-ion diffusion coefficient \((i = p, i = s\) and \(i = n\) in positive and negative electrode and separator
- **D_{Mg+2}** Mg-ion solid diffusion coefficient
- **E_{ref}** Reference potential
- **f** Electrolyte salt activity coefficient
- **F** Faraday’s constant
- **i_{eq}** Equilibrium exchange current density
- **I_{app}** Applied current density
- **I_{G}** Applied GITT current
- **J_{loc,i}** Local current density \((i = p\) and \(i = n\) in positive and negative electrode
- **J_i** pore-wall flux density \((i = p\) and \(i = n\) in positive and negative electrode
- **k_0** Rate constant
- **L_i** Thickness of the electrode and separator \((i = p, i = s\) and \(i = n\)
- **n** electrons transferred in the electrochemical reaction
- **N_{f,i}** Concentration of solute in ionomer solution
- **N_r** Concentration of solvent in ionomer solution
- **r** Total number of ionomer groups
- **R** Universal gas constant
- **r_p** Particle radii
- **S** BET Surface Area
- **s_k** Reactant stoichiometric coefficient
- **S_{hi}** Surface area per unit volume \((i = p\) and \(i = n\) in positive and negative electrode
- **t** Time
- **t_{D,i}** Mg-ion transference number
- **T** Temperature
- **V_{C,i}** Compressed volume
- **V_{M,i}** Molar volume
- **V_{void}** Void volume
- **X** Cell coordinate
- **Y** Dimensionless particle radii
- **w_i** Weight of each component in positive electrode mixture \((i = Bi, C \& PVDF)
- **z_{pi}** Reactant ion charge number

### Greek Symbols

- **\(\alpha_i\)**, **\(\alpha_C\)** transfer coefficients
- **\(\gamma_i\)** Solid-phase Bruggeman coefficient \((i = p\) and \(i = n\) in positive and negative electrode
- **\(g\)** Volume fraction of electrolyte
- **\(e_i\)** Volume fraction of each component in positive electrode mixture \((i = Bi, C \& PVDF)
- **\(g_{i,i}\)** Filler volume fraction of each component in positive electrode mixture \((i = Bi, C \& PVDF)
- **\(\kappa_{i,j}\)** Electrical conductivity of each component in positive electrode mixture \((i = Bi, C \& PVDF)
- **\(\rho_i\)** Electrolyte conductivity
- **\(\mu_i\)** Tap density of each component in positive electrode mixture \((i = Bi, C \& PVDF)
- **\(U_{a,s}\)** Active cations per electrolyte salt molecule
- **\(\psi\)** Total ions per electrolyte salt molecule
- **\(\Phi\)** Concentration cell potential
- **\(\Phi_{i,j}\)** Electric potential \((i = p\) and \(i = n\) in positive and negative electrode
- **\(\Phi_{i,j}\)** Electric potential \((i = p, i = s\) and \(i = n\) in positive and negative electrode and separator

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