A Physics-Based Model Capacity Fade Analysis of LiMn$_2$O$_4$/Graphite Cell at Different Temperatures

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The capacity fading behavior of a LiMn$_2$O$_4$/graphite lithium ion cells at different temperatures is analyzed using a physics-based porous composite electrode model and a parameter estimation technique. The parameter estimation technique is used to extract capacity fade dependent model parameters from experimental cycling data. Although the capacity fading mechanism of the LiMn$_2$O$_4$/graphite lithium ion cells are greatly influenced by temperature, major capacity fading mechanism is closely related to the trapping of Li ions into solid electrolyte interphase on the graphite negative electrode and the reduction in the volume fraction of the active material in the LiMn$_2$O$_4$ positive electrode. At 25°C, the dominant capacity fading mechanism is the formation of the solid electrolyte interphase while at 60°C the dominant capacity fading mechanism is the reduction in the volume fraction of the positive active material. The efficacy of the physics-based composite electrode model is validated with experimental discharge profiles obtained from cells cycled at 25 and 60°C.

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Manuscript submitted September 20, 2018; revised manuscript received October 30, 2018. Published November 29, 2018. This paper is part of the JES Focus Issue of Selected Papers from IMLB 2018.

Lithium ion batteries (LIBs), owing to their significant increase in energy and power densities,$^1$–$^4$ have gained an outstanding acceleration in the worldwide battery market over the past few years and its market share is expected to increase even at a higher pace in the near future as the market size of electric vehicles (EVs) expands.$^6$ Hence, the environment-related issues of this technology are an important factor that needs to be considered for the development of LIBs. On the part of the positive electrode, a more environmental-friendly approach involves the replacement or elimination of cobalt, which is considered as an unfavorable material$^7$ or the use of cobalt free positive electrode materials.

Over the past decade, spinel LiMn$_2$O$_4$ has gained an immense attention owing to its excellent qualities as a positive electrode material, including low cost, high safety, a high discharge voltage plateau (≈4.0 V vs Li/Li$^+$) and facile production. In addition, spinel LiMn$_2$O$_4$ does not contain cobalt, which makes it an environmentally friendly active material. The profound qualities of spinel LiMn$_2$O$_4$ makes it a suitable candidate for EVs and hybrid electric vehicle (HEVs) applications. However, spinel LiMn$_2$O$_4$ suffers from a capacity fade upon prolonged cycling and extended storage at higher temperatures over 55°C, particularly when graphite is used as the negative electrode.$^8$–$^9$

In the quest to enhance the cycle performance of the spinel LiMn$_2$O$_4$ positive electrode material, an intensive effort has been utilized in unveiling and combating the factors responsible for the severe capacity fading.$^{10}$–$^{14}$ So far, apart from the common capacity fading mechanisms in LIBs such as the formation of the solid electrolyte interphase (SEI) at the negative electrode, additional mechanisms have been discovered for the spinel LiMn$_2$O$_4$ positive electrode material in previous years. These mechanisms include the dissolution of the LiMn$_2$O$_4$ active material via Mn(III) disproportionation reaction to form a more stable Mn(IV) and soluble Mn(II) species$^{15}$ and decomposition of the electrolyte via an oxidation process to form the positive electrode electrolyte interphase (CEI).$^{16,17}$ Also, the destruction and reformation of the SEI on the carbonaceous negative electrode by the dissolve Mn(II) ions in the electrolyte has been considered as the most critical mechanism that leads to capacity fading.$^{16}$–$^{18}$

Based on the above listed capacity fading mechanisms, many capacity fade models have been developed to describe the cycle performance of the spinel LiMn$_2$O$_4$ positive electrode material in the past decade.$^{19}$–$^{23}$ Park et al.$^{20}$ developed a mathematical model to describe the cycle performance of spinel LiMn$_2$O$_4$ based on the Mn(III) disproportionation reaction proposed by Lu et al.$^{14}$ The authors modeled the cycle performance via a reduction in the volume fraction of the positive electrode active material due to the dissolution of Mn(II) into the electrolyte. A more advanced pseudo two-dimensional thermal model was developed by Cai et al.$^{19}$ Therein, the shrinking core model was used to describe the solid phase diffusion in the positive electrode and capacity fade was due to an increase in the internal resistance due to the formation inactive material in the positive electrode.

Recently, a comprehensive mathematical model that accounts for the formation and dissolution of SEI on the negative electrode, the formation of CEI at the positive electrode and the dissolution of Mn(II) in the positive electrode to describe the cycle performance of spinel LiMn$_2$O$_4$/graphite cell chemistry was developed by our group.$^{25}$ The formation of the SEI and CEI leads to the loss of Li ions inventory in the both electrodes as well as an increase in the cell resistance while the dissolution lead to a reduction in the positive electrode active material. These models are classified as physico-chemical models and are good for parameter studies and useful for describing capacity-fading mechanism. However, they are very complex and difficult to parameterize.$^{24}$

From the previously developed capacity fade model for spinel LiMn$_2$O$_4$, the cycle performance was described by the loss of Li ions to SEI formation leading to an increase in the internal resistance of the cell and the reduction in the volume fraction of the positive electrode active material due to Mn(II) dissolution. Zhang et al.$^{25}$ performed a capacity fade analysis of a lithium ion cell comprising LiNiO$_2$ positive electrode and a carbon negative electrode using a physics-based single particle model. The authors postulated that, the capacity fade of LIBs due to SEI formation and loss of positive electrode active material can be studied via the changes of three parameters in the physics-based model, namely, the initial state of charge (SOCs) for the positive electrode and negative electrode ($x_{\text{pos}}$ and $x_{\text{neg}}$) and the volume fraction of the positive electrode ($x_{\text{vol}}$). However, they did not use this approach to study the capacity fading mechanism at elevated temperatures because they employed the single particle physics-based model, which does not account for electrolyte decomposition at high temperatures. Lam et al.$^{26}$ also adopted a physics-based pseudo-2D lithium ion battery model to analyze the effect of discharge current density on the degradation mechanism of a generic Li-ion battery. The cycle performance of the cells were described by the fluctuation in the
identified three parameters (the initial state of charge (SOCs) for the positive electrode and the negative electrode ($x_{\text{pos}}$ and $x_{\text{neg}}$) and the volume fraction of the positive electrode ($x_{\text{pos}}$)) as cycling proceeds. Just like Zhang et al., Lam et al. also did not consider the effect of temperature on their analysis.

To the best of our knowledge, there have been no reports on the analysis of capacity fade at different temperatures based on the changes in the initial state of charge (SOCs) of the positive and negative electrode ($x_{\text{pos}}$, $x_{\text{neg}}$, and $x_{\text{vol}}$), and the volume fraction of the positive electrode ($x_{\text{pos}}$) which are known to change with cycling for the LiMn$_2$O$_4$/graphite cell. Hence, in this study, we will conduct a capacity fade analysis of LiMn$_2$O$_4$/graphite cell via the changes in the initial state of charge (SOCs) for the positive electrode and the negative electrode ($x_{\text{pos}}$, $x_{\text{neg}}$, and $x_{\text{vol}}$) and the volume fraction of the positive electrode ($x_{\text{pos}}$) using a physics-based porous composite electrode model at 25 and 60 °C. The physics-based porous composite electrode model accounts for the electrolyte while the single particle model does not, which makes it a better option for capacity analysis at different temperatures and current rates.

### Mathematical Model

The experimental discharge capacity retention at 25 and 60 °C for a 2032 coin-type Li ion cell comprising LiMn$_2$O$_4$ as the positive electrode and artificial graphite as the negative electrode is presented in Figure 1. We used a polyethylene separator (ND420, Asahi Kasei E-Materials, Japan) and a liquid electrolyte consisting of 1.15 M LiPF$_6$ in an ethylene carbonate and ethylmethyl carbonate mixture (3/7 v/v, ENCHEM, Korea). The mass composition of the positive electrode was 90 wt% LiMn$_2$O$_4$ (Iljin Materials, Korea), 5 wt% electric conductor (Super P Li, Imerys, Belgium) and 5 wt% poly(vinylidene fluoride) (PVdF, KF-1300, Kureha, Japan) as a binder. N-methyl pyrrolidone (NMP, Sigma Aldrich, USA) was used as the solvent for electrode slurry. The anode composition was 95 wt% artificial graphite (Showa Denko, Japan), 1 wt% electric conductor (Super P Li, Imerys, Belgium), 4 wt% PVdF (Solef6020, Solvay, France). The cycling performance of the cells were conducted at 1C charge/discharge and a lower and upper cut-off voltage of 3.0 and 4.2 V, respectively. The discharge data were studied using the porous composite electrode model originally built by Newman and Tiedemann 27 and later upgraded by other researchers. 28-30 In general, the porous composite electrode model is based on the material balances on the solid-phase of the two electrodes and on the electrolyte, which considers the involvement of Li ions in all the reaction, and Ohm’s law in the solid and liquid phases. The electrochemical reactions occurring at the surfaces of the electrodes were described by the Butler-Volmer equation for Li-ion intercalation/deintercalation reaction. The set of equations used in the porous composite electrode model and their boundary conditions are presented in Table I. Energy balance equations were not included in this model because, all the simulations were done at low current density where the temperature across the cell does not change significantly at a given operating temperature.

### Results and Discussion

#### Parameter estimation.—To evaluate the parameters that changes with cycling, we compared the experimental voltage profiles obtained from the 2032 coin-type cells at 25 and 60 °C to those from the physics-based model predictions at selected cycle numbers. The outcome of the comparison are shown in Figure 2. The model predictions were made with the parameters in Table II. The correlation between the experimental voltage profiles and those of the physics-based model predictions are quite high. This is evidenced by the lower estimated standard deviation as shown in Figure 2.

The high correlation between the experimental voltage profiles and the physics based model predictions at the two temperatures in Figure 2 were achieved by using a non-linear least square method to estimate the three parameters considered to change with capacity fade in this study. These parameters are the initial SOCs for the positive and negative electrode ($x_{\text{pos}}$, $x_{\text{neg}}$) at the beginning of charging and the volume fraction of the positive electrode ($x_{\text{pos}}$). The changes

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**Figure 1.** The experimental discharge capacity retention of LiMn$_2$O$_4$/graphite cells as a function of number of cycles at 25 and 60 °C. The cells were cycled at 1C and an upper and lower cut of 3.0 and 4.2 V.

**Figure 2.** Comparison of experimental discharge profiles and model-prediction for 1st, 100th, 200th, 300th and 400th at (a) 25 °C and (b) 60 °C.
Table I. Model equations, initial and boundary conditions for the PCEM: An overview.

| Cell compartment | Balance | Governing equations | Boundary or initial condition |
|------------------|---------|---------------------|-----------------------------|
| Anode            | Material, solid phase | $\frac{\partial c_{a,n}}{\partial t} = D_{a,n} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_{a,n}}{\partial r} \right)$ | $c_{a,n}|_{r=0} = c_{a,ini} - D_{a,n} \frac{\partial c_{a,n}}{\partial r}|_{r=0} = 0,$ $-D_{a,n} \frac{\partial c_{a,n}}{\partial r}|_{R_{p,a}} = \dot{j}_n$ |
|                  | Charge, solid phase | $\frac{\partial \dot{j}_n}{\partial r} \left( \frac{\partial c_{a,n}}{\partial r} \right) = a_{c,n} F \dot{j}_n$ | $\sigma_{a,n}|_{x=L_a} = 0 - D_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a} = 0$ |
|                  | Material, liquid phase | $\frac{\partial c_{a,n}}{\partial t} = \frac{\partial}{\partial r} \left( D_{eff,a,n} \frac{\partial c_{a,n}}{\partial r} \right) + (1 - \epsilon_s) \rho_{d,a} \dot{j}_n$ | $c_{e}|_{x=0} = c_{e,0} - D_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a} = 0$ $-D_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a} = -D_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a}$ |
|                  | Charge, liquid phase | $-\frac{\partial}{\partial r} \left( \kappa_{eff,a,n} \frac{\partial \dot{j}_n}{\partial r} \right) + \frac{2RT(1-\epsilon_s^2)}{F} \frac{\partial \kappa_{eff,a,n}}{\partial r} = a_{c,n} F \dot{j}_n$ | $-\kappa_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a} = 0 - \kappa_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a} = \frac{\partial \dot{j}_n}{\partial r}|_{x=L_a}$ |
|                  | Butler-Volmer equation | $\dot{j}_n = k_B (c_{a,n,\max} - c_{n,\text{surf}}) \frac{\dot{\phi}}{0.5} \frac{c_{n,\text{surf}}}{c_{a,n}} \epsilon_{\text{vol}} \left[ \exp \left( \frac{0.5F}{RT} \eta \right) - \exp \left( -\frac{0.5F}{RT} \eta \right) \right]$ | $c_{e}|_{x=0} = c_{e,0} - D_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a} = 0$ $-D_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=L_a} = -D_{eff,a,n} \frac{\partial c_{a,n}}{\partial x}|_{x=(L_a+L_s)}$ |
| Separator         | Material, liquid phase | $\frac{\partial c_{a,p}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_{eff,a,p} \frac{\partial c_{a,p}}{\partial r} \right)$ | $c_{p,\text{ini}}|_{x=0} = c_{p,\text{ini}} - D_{eff,a,p} \frac{\partial c_{a,p}}{\partial x}|_{x=L_a} = 0$ $-D_{eff,a,p} \frac{\partial c_{a,p}}{\partial x}|_{x=(L_a+L_s)} = 0$ $-D_{eff,a,p} \frac{\partial c_{a,p}}{\partial x}|_{x=(L_a+L_s)} = 0$ |
|                  | Charge, liquid phase | $-\kappa_{eff,a,p} \frac{\partial \dot{j}_p}{\partial r} + \frac{2RT(1-\epsilon_s^2)}{F} \frac{\partial \kappa_{eff,a,p}}{\partial r} = a_{c,p} F \dot{j}_p$ | $c_{p,\text{ini}}|_{x=0} = c_{p,\text{ini}} - D_{eff,a,p} \frac{\partial c_{a,p}}{\partial x}|_{x=L_a} = 0$ $-D_{eff,a,p} \frac{\partial c_{a,p}}{\partial x}|_{x=(L_a+L_s)} = 0$ $-D_{eff,a,p} \frac{\partial c_{a,p}}{\partial x}|_{x=(L_a+L_s)} = 0$ |
|                  | Butler-Volmer equation | $\dot{j}_p = k_B (c_{p,\text{max}} - c_{p,\text{surf}}) \frac{\dot{\phi}}{0.5} \frac{c_{p,\text{surf}}}{c_{p,\text{max}}} \epsilon_{\text{vol}} \left[ \exp \left( \frac{0.5F}{RT} \eta \right) - \exp \left( -\frac{0.5F}{RT} \eta \right) \right]$ |

Table II. Design parameters, electrode specific parameters, and other constants used in this study.

| Design parameters | Li$_3$Mn$_2$O$_4$ | Li$_3$C$_6$ |
|-------------------|------------------|------------|
| Electrode thickness, μm$^a$ | 36 | 43 |
| Volume fraction electrolyte$^b$ | 0.33 | 0.37 |
| Maximum solid phase concentration, mol m$^{-3}$ | 23230 | 27362 |
| Initial SOC of the electrode | 0.45 | 0.58 |
| Volume fraction of active material | 0.559 | 0.566 |
| Reaction rate constant, mol m$^{-2}$ s$^{-2}$ | $3.94 \times 10^{-11}$ | $3 \times 10^{-11}$ |
| Density g/cm$^3$ | 4.2 | 2.2 |
| Matrix conductivity, S/m$^b$ | 10 | 100 |
| Separator thickness, mm$^b$ | 20 | 20 |
| Separator porosity$^b$ | 0.41 | 0.41 |
| Initial salt concentration, M$^b$ | 1.15 | 1.15 |
| Diffusion coefficient, m$^2$/s$^c$ | $3.98 \times 10^{-14}$ | $1.14 \times 10^{-14}$ |
| Particle radius, μm$^a$ | 6.5 | 10.5 |

$^a$Value set in cell design.
$^b$Parameters based on literature value.$^{24}$
$^c$Parameters not based on literature value.
in the parameters with cycling at 25 and 60°C is illustrated in Figure 3. The volume fraction of the positive electrode ($\varepsilon_{\text{pos}}$) decreased with cycling with the rate of decrease being higher at 60°C (Figure 3a). Also, the initial SOC for the positive electrode ($x_{0,\text{pos}}$) increased with cycling for the two temperatures (Figure 3b). The rate of increase was rapid at 60°C. On the other hand, a different trend was observed for initial SOC for the negative electrode ($x_{0,\text{neg}}$), that is, it changed with cycling at 25°C but it did not show any significant changes at 60°C. Figure 3 demonstrates that, during cycling, both the positive and negative electrodes become frequently less charged at 25°C while at 60°C, only the positive electrode becomes less charged.

The predicted SOCs for the positive and negative electrodes at the end of discharge (EOD) ($x_{\text{pos}}$ and $x_{\text{neg}}$) and, at 25 and 60°C are shown in Figure 4. At 25°C (Figure 4a), the negative electrode becomes less discharged while the positive electrode shows no relevant changes at the EOD ($x_{\text{neg}}$ increases while $x_{\text{pos}}$ remains constant). The SOC of the positive electrode remained constant at ca. 0.98, stipulating that the positive electrode is almost completely intercalated. A similar pattern was observed in the intercalation of the negative electrode of the cells cycled at 60°C (Figure 4b), however, unlike the intercalation pattern in the positive electrode at 25°C, that at 60°C became less intercalated ($x_{\text{pos}}$ decreases). In addition, the rate at which the negative electrode becomes less discharged at the EOD is more severe at 60°C than at 25°C. A detail discourse of the difference in the patterns at the two temperatures are given in Analysis of capacity fade section.

**Model prediction.**—We fitted the model parameters to the quadratic equations presented in Table III. The initial SOC for the negative electrode at 60°C ($x_{\text{neg}}$) was not included in Table III because it did not change with cycling. The various fitting parameters of the equation presented in Table III were obtained using the curve-fitting tool in Matlab. The parameters extrapolated from the model equations are depicted in Figure 5. The parameter extrapolation was made based on the assumption that, the capacity fading mechanism is not altered during the duration of our prediction.

The extrapolated model parameters in Figure 5 were used to predict the discharge capacity retention as a function of cycle number at 25 and 60°C. The model predictions of the discharge capacity retention for 1000 cycles at the 25 and 60°C are shown in Figure 6. The experimental discharge capacity retention for 400 cycles were compared with the model prediction at 25 and 60°C and are also shown in Figure 6a and 6b, respectively. There was a good agreement between the experimental data and the model predictions. A prediction of the discharge capacity retention by an empirical model (Table IV) at 25 and 60°C have also been demonstrated in Figure 6. At 25°C (Figure 6a), the predicted discharge capacity retention by the physics-based model at the end of the 1000th cycle was quite higher...
than that predicted by the empirical based model. This is in contrast to the previous report made by Zhang et al.\textsuperscript{25} when they compared a single-particle physics-based model prediction of discharge capacity of a 1 Ah LiNiCoO\textsubscript{2}/carbon lithium ion cell to that of an empirical single-particle physics-based model prediction of discharge capacity before it got to the 700th cycle, while for the physics-based model, the equation at 25\textdegree C. This contrast can be attributed to the different cell designs and the active material of the positive electrode employed in the two studies. A similar trend was also observed at 60\textdegree C in Figure 6b. For the empirical equation prediction, the cell completely died before it got to the 700th cycle, while for the physics-based model, the cell lasted to ca. 900\textdegree C cycle.

Figure 7 shows the predicted SOCs of the positive and negative electrode at the EOD using the estimated model parameters. The predicted SOC of the positive electrode at the EOD at 25\textdegree C (Figure 7a) remained unchanged, which is similar to that observed in the first 400 cycles in Figure 4. That of the negative electrode also continued to increase until the 1000th cycle. Increasing the temperature to 60\textdegree C in Fig. 7b accelerated the rate at which the SOC of the negative electrode at the EOD increased (less discharged). The SOC of the positive electrode at the EOD also begun to decrease (less intercalated) until the 800th cycle where it remained constant. The detailed analysis of the capacity fade of the LiMn\textsubscript{2}O\textsubscript{4}/graphite cells at 25 and 60\textdegree C based on the information derived by using the physics-based model will be presented in the following section.

Analysis of capacity fade.—From the results presented in the previous section, it is clearly seen that, temperature has a profound effect on the capacity fading mechanism of the LiMn\textsubscript{2}O\textsubscript{4}/graphite cells. The phenomenon constituting these changes are discussed in this section.

The study conducted on the variation of the parameters with cycling indicates that the volume fraction of the active material in the positive electrode (\(\varepsilon_{\text{pos}}\)) decreases as cycling proceeds with the rate of decrease being accelerated at a higher temperature (see Figure 3). This postulates that, the positive electrode loses some of the active material during cycling and the loss is high at higher temperatures. For the, LiMn\textsubscript{2}O\textsubscript{4}/graphite cells, the loss of active material has been attributed to the dissolution of the Mn(II) due to the disproportionation reaction of Mn(III) into soluble Mn(II) species and stable Mn(IV) species.\textsuperscript{31–33} Experimentally, it has been reported that, increasing the temperature increases the rate of Mn dissolution in the positive electrode resulting in a fatal capacity decay of the cells.\textsuperscript{8,33–36} Hence, the results obtained in our parameter estimation analysis of the capacity fade at the two given temperatures are in line with that of previously reported experimental results.

In addition, there have been several previous reports on the occurrence of side reactions on the negative graphite electrode during charging process.\textsuperscript{17,28} These side reactions are known to consume Li ions giving rise to the formation of the SEI on the surface of the negative graphite electrode. In this study, the loss of the Li ions can be envisioned in the variation of the both the initial SOCs and that at the EOD of the positive and negative electrode. Owing to the relatively high rate of the SEI formation on just produced cells, the loss of Li ions to the formation of the SEI controls the capacity fade during the first few cycles (pre-cycling).\textsuperscript{38} However, the capacity fade analysis in this study was conducted after the pre-cycling stage; hence, the quantitative estimation of the Li ions loss to the SEI formation during the first stage was not done. Nevertheless, during the entire cycling at 25\textdegree C, the SOC of the positive electrode (\(x_{\text{pos}}\)) did not change. Notwithstanding, the negative electrode became increasingly less intercalated at the EOD. That is, there is a progressive deposition of Li ions in the graphite negative electrode that cannot be intercalated back into the positive electrode. In addition, the residual capacity of the positive electrode decreases as cycling proceeds with the rate of decrease being accelerated at a higher temperature (see Figure 3). This postulates that, the positive electrode loses some of the active material during cycling and the loss is high at higher temperatures. Here the positive electrode is the limiting electrode because it is almost completely discharged at EOD, causing the cell to reach the lower cut-off voltage.

The capacity-fading mechanism at 60\textdegree C is slightly different from that at 25\textdegree C. That is, there was a continuous trapping of Li ions in graphite electrode at a rapid rate throughout the entire cycling (rapid increase in in Figure 7b). In addition to that, the positive electrode was progressively less intercalated at the EOD, resulting in a

\begin{table}[ht]
\centering
\caption{Mathematical expression used for the extrapolation in Figure 5.}
\begin{tabular}{lcccr}
\hline
Parameters & Expression & \hspace{2cm} & a & b & C \\
\hline
\(x_{\text{pos},25\textdegree C}\) & \(ax^b + c\) & \hspace{2cm} & \(-1.005 \times 10^{-4}\) & 1.000 & 1.000 \\
\(x_{\text{pos},25\textdegree C}\) & \(ax^b + c\) & \hspace{2cm} & \(1.138 \times 10^{-2}\) & 0.1412 & 0.9892 \\
\(x_{\text{neg},25\textdegree C}\) & \(ax^b + c\) & \hspace{2cm} & \(-9.526 \times 10^{-4}\) & 0.6694 & 1.001 \\
\(x_{\text{pos},60\textdegree C}\) & \(ax^b + c\) & \hspace{2cm} & \(-1.005 \times 10^{-4}\) & 0.796 & 1.006 \\
\(x_{\text{neg},60\textdegree C}\) & \(ax^b + c\) & \hspace{2cm} & \(5.81 \times 10^{-3}\) & 0.6557 & 0.9986 \\
\hline
\end{tabular}
\end{table}
Figure 5. Extrapolation of the model parameters presented in Figure 3. The mathematical expressions used for the extrapolation are presented in Table III.

decreasing of the SOC of the positive electrode ($x_{pos}$) at the EOD. However, the initial SOC of the negative electrode ($x_{0,neg}$) remained constant. This is due to the rapid reduction in the holding capacity of the positive electrode as the positive electrode loses more active material. In return, more usable Li ions are accumulated inside the negative electrode, casing fatal capacity decay. Thus, the loss of Li ions, which leads to a sudden increase in the SOC of the negative electrode ($x_{neg}$) at EOD, is not only due to SEI formation, but also due to a significant reduction in the holding capacity of the positive electrode. This makes it impossible for the intercalated Li ions into the negative electrode to de-intercalate back into the positive electrode. This is supported by the negligible changes in the initial SOC of the negative electrode ($x_{0,neg}$). Experimentally, it has been reported that, at elevated temperatures, the dissolve Mn(II) migrate through the separator to the graphite where they are reduced to metallic Mn nanoparticles. The Mn nanoparticles act as catalyst perpetuating the rapid decomposition of the electrolyte to form the SEI on the surface of the negative electrode during cycling.$^{17,39,40}$ The formation of the SEI leads to a continuous trapping of the usable Li ions resulting in a drastic capacity decay.$^{18,41}$ This is evidenced in the reduction of the SOC of the positive electrode as observed in Fig. 7b. At the last 200 cycles, the capacity mechanism at 60°C slightly changes. The rate of Li ion trapping due to SEI formation continuously increased with cycling and the positive electrode became the limiting electrode ($x_{pos}$ remained constant).

Conclusions

The capacity fading characteristics of a LiMn$_2$O$_4$/graphite lithium ion cells was analyzed by fitting the model predictions of a physics-based porous composite electrode model to experimental discharge profiles obtained from cycling the cells at 25 and 60°C. The parameters that changed with cycling were estimated using a nonlinear

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Table IV. Empirical model expressions.

| Temperature | Model          | A     | B       | C       | D     |
|-------------|----------------|-------|---------|---------|-------|
| 25°C        | $Ax^B + Cs + D$ | -3.676| 0.1801  | -0.02398| 103.3 |
| 60°C        | $Ax^B + Cs + D$ | -1.434| 0.7124  | 0.07247 | 100.5 |
least square technique. The analysis conducted on the experimental discharge profiles showed that, the capacity fading mechanism of the LiMn$_2$O$_4$/graphite lithium ion cells were affected by temperature. The major capacity fading mechanism observed based on our parameter estimation analysis is the trapping of the cyclable Li ions into the SEI on the negative electrode and reduction in the volume fraction of the active material in the positive electrode. The positive electrode was the limiting electrode at 25°C. At 60°C, the reduction in the volume fraction of the active material occurred at a rapid rate and the positive electrode became less intercalated at the end of discharge. There was also a rapid trapping of Li ions to the formation of the SEI due to the presence of the Mn nanoparticles at the graphite negative electrode.

**Acknowledgment**

This research was supported by Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science & ICT (NRF-2017M1A2A2044493) and the international Collaborative Energy Technology R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea.

**List of Symbols**

- $a_{ij}$: specific surface area of electrode $i$ ($i = p, n$), m$^{-1}$
- $c_e$: concentration of electrolyte, molm$^{-3}$
- $c_{s,i}$: concentration of lithium ions in the solid phase of electrode $i$ ($i = p, n$), molm$^{-3}$
- $c_{s,i,ini}$: initial concentration of lithium ions in the solid phase of electrode $i$ ($i = p, n$), molm$^{-3}$
- $c_{s,i,max}$: maximum concentration of lithium ions in the solid phase of electrode $i$ ($i = p, n$), molm$^{-3}$
- $D$: electrolyte diffusion coefficient, m$^2$s$^{-1}$
- $D_{i,i}$: lithium ion diffusion coefficient in the solid phase of electrode $i$ ($i = p, n$), molm$^{-3}$
- $F$: Faraday’s constant, 96487 Cmol$^{-1}$
- $j$: pore wall flux of lithium ions, molm$^{-2}$s$^{-1}$
- $k_i$: intercalation/deintercalation reaction rate constant of electrode $i$ ($i = p, n$), m$^2$mol$^{-1}$s$^{-1}$
- $L_n$: thickness of negative electrode, m
- $L_p$: thickness of separator, m
- $L_{pp}$: thickness of positive electrode, m
- $r$: radial coordinate, m
- $R_i$: radius of active material of electrode $i$ ($i = p, n$), m

(No. 20158510050020). We are also very thankful for the support from the DGIST Supercomputing and Bigdata Center.
\( R_{SEI} \) film resistance at the electrode/electrolyte interface, \( \Omega \text{m}^2 \)
\( t_0 \) cation transference number
\( T \) ambient temperature, K
\( U_0 \) equilibrium potential, V

**Greek**

\( \varepsilon \) volume fraction
\( \eta \) local over potential, V
\( \kappa \) ionic conductivity of the electrolyte, Sm\(^{-1}\)
\( \sigma_i \) electronic conductivity of the solid phase of electrode \( i \) (\( i = p, n \)), Sm\(^{-1}\)
\( \phi_1 \) solid phase electric potential, V
\( \phi_2 \) solution phase electric potential, V

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