Cubic Spline Regression for the Open-Circuit Potential Curves of a Lithium-Ion Battery

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A cubic spline regression model was used to fit the experimental open-circuit potential (OCP) curves of two intercalation electrodes of a lithium-ion battery. All the details of an OCP curve were accurately predicted by the resulting model. The number of regression intervals used to fit an OCP curve was determined in a way such that in each regression interval the OCP exhibits a profile predictable by a third-order polynomial. The locations of the data points used to separate regression intervals were optimized. Compared to a polynomial model with the same number of fitting parameters, the cubic spline regression model is more accurate. The cubic spline regression model presented here can be used conveniently to fit complicated profiles such as the OCP curves of lithium-ion battery electrodes.

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The dependence of the open-circuit potential (OCP) of an intercalation electrode in a lithium-ion battery on the lithium concentration of that electrode cannot be explained by a general Nernst equation. Because of this, the equations used in the literature to fit the experimental OCP curve (the dependence of the OCP on the concentration of lithium in the solid phase) of an intercalation electrode vary wildly. For instance, Doyle et al.1 used an equation having two exponential terms and a constant term to fit the experimental OCP curve of a petroleum coke carbon electrode, Ramachandran et al.2 used a rational expression to fit the experimental OCP curve of a carbon electrode of a Sony 18650 cell, and Verbrugge and Koch3 used a modified Nernst equation to fit the experimental OCP curve of a single-fiber carbon electrode. Among those equations, the first two are empirical in nature, and the last one is physically meaningful but can only be used for a few intercalation electrodes having a well-ordered material structure. If the experimental OCP curve of an intercalation electrode exhibits some voltage plateaus corresponding to different staging processes, which is the case for most intercalation electrodes,4-7 the equations found in the literature are not as accurate as desired.

The Butler-Volmer equation (see Eq. 3 of Ref. 2) used to predict the rate of the electrochemical reaction at an electrode in a lithium-ion battery depends exponentially on the difference between the working potential (the potential difference between the solid phase and solution phase) and the OCP of the electrode. If one is interested in estimating the rate constant of the Butler-Volmer equation from a voltage vs. time discharge curve, any small inaccuracy in knowing the electrode OCP may cause significant error in the estimated value of the rate constant. Therefore, fitting accurately the OCP curve of an intercalation electrode is important to us. On the experimental OCP curve of a carbon electrode with a graphite structure, there are some closely spaced voltage plateaus near 0.1 V (vs. Li metal), and each voltage plateau corresponds to a particular range of lithium intercalation in that electrode.8-11 If the capacity fade of a carbon electrode occurs continuously with cycling due to the branching of charge current to the solvent reduction side reaction,12 one can expect that the carbon electrode will never reach a structure of LiC6 (fully charged carbon electrode) in its lifetime, and the voltage plateau corresponding to that structure on a low rate discharge curve of that electrode will become narrower and narrower with cycling.Attributing the capacity fade of a lithium-ion battery to the side reaction on its carbon anode may be justified by such a change in the voltage plateau.

Considering that, in general, the experimental OCP curve of an intercalation electrode has a profile much more complicated than that predicted by a general Nernst equation, an empirical equation is desired to fit such curves. Unfortunately, most empirical equations available in the open literature for that purpose are highly nonlinear in nature with respect to their fitting parameters.1-2,10,11 To predict all the voltage plateaus on an OCP curve, an empirical equation may have to include many nonlinear parameters.1-2,10,11 Because of this, providing reasonable initial guesses for all the parameters in such an empirical equation is a challenging mission to guarantee the convergence of nonlinear regression.

In this paper, a cubic spline regression model12,13 was used to fit the experimental OCP curves of two intercalation electrodes, a carbon electrode, and a cobalt oxide electrode. The advantage of using the cubic spline regression model to fit a complicated profile is demonstrated and compared to a polynomial fit.

Cubic Spline Regression Model

The concept of the spline originated from the drafting technique of using a thin, flexible strip called a spline to draw smooth curves through a set of points.14 First, consider spline interpolation.14 The desire is to connect m experimental data points, (x1, y1), (x2, y2), ..., and (xm, ym), by a smooth curve. The curve is divided by those points into m − 1 intervals. Assume in each interval the data points can be represented by a third-order polynomial

\[ y = a_1 + b_1x + c_1x^2 + d_1x^3 \]  [1]

where x is the independent variable, y is the dependent variable, and a1, b1, c1, and d1 are parameters for the ith interval. To define m − 1 intervals completely, 4 × (m − 1) parameters (a1, b1, c1, and d1) need to be determined. Therefore, 4 × (m − 1) equations are required. One can specify 2 × m equations by assuming that Eq. 1 is valid for all the data points (each interior data point is used twice). One can specify another 2 × (m − 2) equation by assuming that both the first and the second derivatives of the dependent variable with respect to the independent variable are continuous at each interior data point. One can specify the other two equations by assuming that the second derivative of the dependent variable is zero at two end points, (x1, y1) and (xm, ym).14 Once all the 4 × (m − 1) parameters are determined, one can use Eq. 1 to interpolate any point within an interval. The procedure described is the so-called cubic spline interpolation.14 Whether one should use a third-order polynomial (cubic spline interpolation) or a second-order polynomial (quadratic spline interpolation) depends on the curvature of the data point trajectory. However, using a higher order polynomial is not commonly done.

Cubic spline interpolation is useful when the number of data points is small. If the number is great and all the data points are closely spaced, unfortunately, spline interpolation is inefficient.

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Cubic spline regression is similar to cubic spline interpolation. In cubic spline regression, a third-order polynomial is also used for each interval, and the dependent variable and its first and second derivatives are also continuous at all the knots (i.e., the points chosen to define regression intervals). The difference between cubic spline regression and cubic spline interpolation is that only a small number of knots is used in cubic spline regression based on the curvature change of the data point trajectory. A graphic illustration of using knots to define regression intervals is given later. In a cubic spline regression model, Eq. 1 is replaced by the general equation:

\[ y = a + bx + cx^2 + dx^3 + \sum_{i=1}^{k} D_i \varepsilon_i (x_i - x) \]

where \( a, b, c, d, \) and \( \varepsilon_i \) are parameters, \( x_i \) is the location of the \( i \)th knot, \( k \) is the number of knots (k knots define \( k + 1 \) regression intervals because end data points are not used as knots), and \( D_i \) is the dummy (or indicator) variable defined to be one in a particular range of \( x \) and to be zero otherwise. Equation 2 is a general equation whose exact form varies from one regression interval to another. The model equation for the first interval usually takes the form

\[ y = a + bx + cx^2 + dx^3 \]

when all the \( D_i \)’s equal zero in the first interval. The model equation for the second interval takes the form

\[ y = a + bx + cx^2 + dx^3 + \varepsilon_i (x - x_i)^3 \]

when \( D_1 = 1 \) in the second interval. The model equation for the third interval takes the form

\[ y = a + bx + cx^2 + dx^3 + \varepsilon_i (x - x_i)^3 + \varepsilon_2 (x - x_2)^3 \]

when both \( D_1 \) and \( D_2 \) equal one. As observed from Eq. 3-5, the model equations used for any two adjacent intervals differ only by one term. The slight difference in model equations for two adjacent intervals is created so that the continuity of the dependent variable \( y \), and the continuities of its first and second derivatives at the knot separating those two intervals are all satisfied automatically (\( x_i \) is the location of the knot separating the first and the second intervals, and \( x_2 \) is the location of the knot separating the second and the third intervals). Because of this, the curve predicted by the cubic spline regression model is expected to be very smooth. Even though, in general, the regression intervals can be numbered from the first to the last in an increasing order of the independent variable \( x \), one may elect to number them in a different way (i.e., the regression intervals are numbered in a decreasing order of \( x \)). In any case, the model equations for every two adjacent intervals must differ by only one term.

Once the number of knots and their locations are known (knots can be points other than the available experimental data points), one can use Eq. 2 and linear least-squares regression to obtain estimates of parameters, \( a, b, c, d, \) and \( \varepsilon_i \). In most cases, the experimental data points can be fitted with a desired accuracy when using some knots picked by eye according to the curvature change of the data point trajectory, even though the coordinates of knots used in the regression may not be the ones giving rise to the best fit of the data. The coordinates of knots can be optimized by treating them as additional fitting parameters in a model. In this case, nonlinear least-squares regression is required (Eq. 2 is nonlinear with respect to \( \varepsilon_i \) and \( x_i \)). If needed, the number of knots and the coordinates of these knots can both be optimized. The number of knots can be optimized by using several consecutive numbers of knots in the regression and the number leading to the best fit is the optimal one.

**Multiple Least-Squares Regression**

Because in cubic spline regression the available experimental data points are divided into a number of regression intervals using knots and each resulting interval has a different form of the model equation, using multiple least-squares regression to obtain parameter estimates is required. That is, the sum of squared residuals, \( \Phi \), is to be minimized:

\[ \Phi = \sum_{i=1}^{k} \sum_{j=1}^{n_i} (y_{ij}^* - y_{ij})^2 \]

where \( n_i \) is the number of available data points in the \( i \)th interval, \( k \) is the number of knots defining \( k + 1 \) intervals, \( y_{ij}^* \) is the experimental value of the dependent variable at the \( j \)th data point of the \( i \)th interval, and \( y_{ij} \) is the predicted value of the dependent variable at the \( j \)th data point of the \( i \)th interval.

In linear regression, minimization of Eq. 6 yields:

\[ \theta^* = \sum_{i=1}^{k} (J_i^T J_i)^{-1} \sum_{j=1}^{n_i} (J_i^T y_i^*) \]

where \( \theta^* \) is the vector of estimates of parameters \( (a, b, c, d, \) and \( \varepsilon_i) \), \( y_i^* \) is the vector of the experimental values of the dependent variable of the \( i \)th interval, and \( J_i^T \) is the transpose of \( J_i \), the Jacobian matrix of the \( i \)th interval.

\[ J_{ik} = \left( \frac{\partial y}{\partial \theta_i} \right)_{x_k} \]

where the subscript \( l \) is used to represent the \( l \)th fitting parameter, \( \theta_i \), and the subscript \( k \) is used to represent the \( k \)th data point in the \( i \)th interval. In linear regression, the final estimates of all the parameters are obtained after evaluating Eq. 7 once.

In nonlinear regression, Eq. 7 is replaced by:

\[ \Delta \theta^* = \sum_{i=1}^{k} (J_i^T J_i)^{-1} [J_i^T (y_i^* - Y_i)] \]

where \( \Delta \theta^* \) is the vector of the incremental values of parameters, and \( Y_i \) is the vector of the predicted values of the dependent variable of the \( i \)th interval. In nonlinear regression, the final parameter estimates are obtained via an iterative procedure using Eq. 9 until either each element in \( \Delta \theta^* \) has a negligible value, or \( \Phi \) (calculated by Eq. 6) does not change appreciably from one iteration to another. At the end of an iteration, \( \Delta \theta^* \) is added to \( \theta^* \) to update the parameter values in \( \theta^* \).

The 95% confidence interval for parameter \( \theta_i \) can be constructed using

\[ \theta_i^* - t_{1-0.025} S_{\theta_i} / \sqrt{n} \leq \theta_i < \theta_i^* + t_{1-0.025} S_{\theta_i} / \sqrt{n} \]

where \( \theta_i^* \) is the point estimate of parameter \( \theta_i \), \( t_{1-0.025} \) is a value of Student’s t distribution with \( n-k-4 \) degrees of freedom (the total numbers of data points and fitting parameters are \( n \) and \( k + 4 \), respectively), \( S_{\theta_i} \) is the \( i \)th element of the principal diagonal of \( [\sum_{i=1}^{k} (J_i^T J_i)]^{-1} \), and \( S_E \) is the standard deviation calculated by

\[ S_E = \sqrt{\frac{1}{n-k-4} \sum_{i=1}^{k} \sum_{j=1}^{n_i} (y_{ij}^* - y_{ij})^2} \]

Equation 10 can be used to judge whether or not a parameter is significant in a linear model. If zero is included in Eq. 10 for parameter \( \theta_i \), one can conclude that parameter is not significant and can be removed from that model. Using Eq. 10 to judge the significance of a parameter in a linear model is equivalent to performing the so-called t-test. One needs to be careful when using Eq. 10 to judge the significance of a parameter in a nonlinear model. In contrast to a linear model, the confidence interval calculated using Eq.
10 for a parameter in a nonlinear model is generally bigger than the region where the true value of that parameter may lie. This is due to the so-called correlations between parameters. If a value of zero is not included in any confidence interval obtained using nonlinear regression, it is safe for one to conclude that all the parameters are statistically important. However, if a value of zero is included in a confidence interval, one cannot simply conclude that parameter is statistically insignificant in the nonlinear model.

Experimental

The experimental OCP curves of a cobalt oxide electrode were measured at room temperature (25°C) using a Swagelok-type half-cell setup consisting of a cobalt oxide electrode, a separator, and a lithium foil electrode (see Fig. 1). A Celgard 2400 polypropylene membrane (Charlotte, NC) having a thickness of 25 μm and a porosity of 0.37 was used as the separator. The cobalt oxide electrode used in this work was supplied by the Mine Safety Appliances Company (Sparks, MD). This electrode, which was fabricated using 91% C-022 LiCoO₂, 4% KS-6 graphite, 2% super-P conductive carbon, and 3% polyvinylidene fluoride (PVDF) loaded on one side of a 20 μm thick aluminum foil, has an average thickness of 69.9 μm and an average material loading of 20.1 mg/cm². A 0.38 mm thick lithium metal foil purchased from Aldrich (St. Louis, MO) was used as the counter electrode, which also serves as the reference electrode. The cobalt oxide electrode used in the half-cell was a round disk having a diameter of 1.27 cm and a theoretical capacity of 0.137 Ah/g was used to calculate the theoretical capacity of the carbon electrode. The cobalt oxide electrode disk, one layer of 25 μm thick Celgard 2300 polypropylene-polyethylene-polypropylene separator (slightly bigger in size than an electrode disk), and one piece of the lithium foil disk were used to assemble the half-cell. The LP 30 Selectipur electrolyte purchased from E. Merck (Hawthorne, NY) with a LiPF₆ concentration of 1.0 M in a 1:1 v/v ethylene carbonate-dimethyl carbonate (EC-DMC) solvent was used to fill the cell. The coin cell was cycled three times using a 500 mA constant current charge process, a 20 mA constant voltage charge process (the cutoff current was 50 μA), and a 500 μA constant current discharge process (the cutoff voltage was 2.0 V). The charge and discharge curves measured in the third cycle were used as the OCP curves of the carbon electrode for a charge process and for a discharge process, respectively.

In this work, the OCP was first recorded vs. Qₑ, the charge capacity in Ah, or vs. Qₐ, the discharge capacity in Ah. Then Qₑ or Qₐ was converted to 1, a dimensionless state of charge, by

\[
x = \frac{Qₑ}{Q_{\text{theoretical}}} \quad \text{or} \quad x = \frac{Q_{\text{total}} - Qₐ}{Q_{\text{theoretical}}} \tag{12}
\]

for the carbon electrode assumed to have a structure of Li₅C₆, or by

\[
x = 1 - \frac{Qₑ}{2Q_{\text{theoretical}}} \quad \text{or} \quad x = 1 - \frac{Q_{\text{total}} - Qₐ}{2Q_{\text{theoretical}}} \tag{13}
\]

for the cobalt oxide electrode assumed to have a structure of LiₓCoO₂. In Eq. 12 and 13, Q_{\text{theoretical}} stands for the theoretical capacity of the intercalation electrode in ampere-hours, and Q_{\text{total}} and Q_{\text{total}} stands for the total charge and discharge capacities in ampere-hours, respectively. To obtain Eq. 12 and 13, we assume that the fully discharged cobalt oxide electrode has a dimensionless concentration of 1 and a structure of LiₓCoO₂, and the fully discharged carbon electrode has a dimensionless concentration of 0 and a structure of C₆. When Q_{\text{total}} = Q_{\text{total}} = Q_{\text{theoretical}}, the fully charged carbon electrode has a dimensionless concentration of 1 and a structure of LiC₆, and the fully charged cobalt oxide electrode has a dimensionless concentration of 1 and a structure of LiₓCoO₂ (in Eq. 13, the value of x ranges from 0.5 to 1).

Results and Discussion

In this work, all the experimental OCP curves were fitted by the cubic spline regression model along with the optimization of the coordinates of knots x. It is important to note that including x in cubic spline regression makes Eq. 2 become nonlinear with respect to its fitting parameters. Therefore, providing reasonable initial
guesses for fitting parameters is important to guarantee the convergence of regression. To fit an experimental curve in this work, two or three consecutive numbers were first tried for \( k \) and the assumed values by eye were used for \( x_i \) values in linear regressions (to start with, \( x_i \) values were excluded from the fitting parameter list). To obtain the final estimates of \( a, b, c, d, e_i \), and \( x_i \), the number for \( k \) leading to a desired accuracy in linear regression and the resulting values of \( a, b, c, d, e_i \), and \( x_i \) were then used as initial guesses in nonlinear regression (\( x_i \) was added to the fitting parameter list).

The experimental OCP curves of the cobalt oxide electrode obtained from both a discharge process and a charge process are presented in Fig. 2. As observed in Fig. 2, these OCP curves exhibit a hysteresis behavior. That is, the OCP curve measured in a low rate charge process does not agree with that measured in a low rate discharge process. Similar phenomena have already been reported in the literature.\(^{17-19}\) The charge/discharge current of 30 \( \mu \)A used in this work to measure an OCP curve of the cobalt oxide electrode was small (lower than 1/100 C rate) and was not expected to cause any significant loss in the half-cell voltage. Such a low rate current has also been used in the literature to measure the OCP curve of an intercalation electrode.\(^{20}\) In this work, the OCP curve of the cobalt oxide electrode measured in a charge process was fitted separately from that measured in a discharge process. For the experimental OCP curve obtained in a discharge process, five knots were used in the regression, and for the experimental OCP curve obtained in a charge process, four knots were used. Using knots to define regression intervals for the experimental OCP curve obtained in a discharge process are presented in Fig. 2. As observed, six regression intervals are defined by five knots, and each resulting regression interval exhibits a profile predictable by a third-order polynomial. The coordinates of all the knots presented in Fig. 2 are initial guesses used in nonlinear regression.

The OCP curves of the cobalt oxide electrode predicted by the cubic spline regression model are compared with the experimental curves in Fig. 3. As observed, two experimental OCP curves were fitted very well. The goodness of fit is also demonstrated in Fig. 4 from the plot of \( y_i^e - y_i^o \) vs. \( x \), the dimensionless state of charge of the cobalt oxide electrode. As observed in Fig. 4, except for a few scatters, \( y_i^o \), the predicted OCP deviates from \( y_i^e \), the experimental OCP, only by a small value (\( \leq 0.003 \) V) at each data point. Moreover, \( y_i^e - y_i^o \) is randomly distributed around a mean of zero. The dummy variables \( D_i \) defined in cubic spline regression are presented in Table I. The exact forms of model equations used in fitting the experimental OCP curve obtained in a discharge process are demonstrated in the Appendix. Table I also presents the 95% confidence intervals for all the fitting parameters. As observed in Table I, a value of zero is not included in any confidence interval. Therefore, all the parameters are statistically significant for the cobalt oxide electrode. The first regression interval was chosen here to be located

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**Figure 2.** The experimental OCP curves of the cobalt oxide electrode obtained in both a charge process and a discharge process.

**Figure 3.** Comparison of the experimental OCP curves of the cobalt oxide electrode and the curves predicted by cubic spline regression. 12-digit numerical precision was used in the regression.

**Figure 4.** Distribution of the regression error in fitting the experimental OCP curves of the cobalt oxide electrode using cubic spline regression.
in the middle region of the data point range rather than at one end. Choosing a middle region as the first regression interval was to avoid round-off error. One may observe from Fig. 2 or 3 that not only is there a steep OCP profile on the rightmost side, but also a fast change in OCP on the leftmost side. If the first regression interval is chosen to be at one end instead, a very negative value of OCP may be neutralized. In contrast, when the first interval is chosen to be in the middle region of the data point range rather than at one end.

Table I. The 95% confidence intervals for all the parameters used in Eq. 2 to fit the OCP curves of the cobalt oxide electrode.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Discharge process</th>
<th>Charge process</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ), the number of knots</td>
<td>( x_1 = 0.95912 \pm 0.00124 )</td>
<td>( x_1 = 0.98167 \pm 0.00060 )</td>
</tr>
<tr>
<td>( x_2 = 0.98829 \pm 0.00600 )</td>
<td>( x_2 = 0.63193 \pm 0.00221 )</td>
<td></td>
</tr>
<tr>
<td>( x_3 = 0.74787 \pm 0.00318 )</td>
<td>( x_3 = 0.56330 \pm 0.00115 )</td>
<td></td>
</tr>
<tr>
<td>( x_4 = 0.54438 \pm 0.00177 )</td>
<td>( x_4 = 0.51672 \pm 0.00117 )</td>
<td></td>
</tr>
<tr>
<td>( x_5 = 0.52170 \pm 0.00233 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( x_i ), the knot coordinate</td>
<td>( x_3 &lt; x &lt; x_4 )</td>
<td>( x_2 &lt; x &lt; x_1 )</td>
</tr>
<tr>
<td>( D_i ), the dummy variable</td>
<td>( D_1 = 1 ) if ( x &gt; x_1 )</td>
<td>( D_1 = 1 ) if ( x &gt; x_1 )</td>
</tr>
<tr>
<td>( D_2 = 1 ) if ( x &gt; x_2 )</td>
<td>( D_2 = 1 ) if ( x &lt; x_2 )</td>
<td></td>
</tr>
<tr>
<td>( D_3 = 1 ) if ( x &lt; x_1 )</td>
<td>( D_3 = 1 ) if ( x &lt; x_1 )</td>
<td></td>
</tr>
<tr>
<td>( D_4 = 1 ) if ( x &lt; x_2 )</td>
<td>( D_4 = 1 ) if ( x &lt; x_2 )</td>
<td></td>
</tr>
<tr>
<td>( a (V) )</td>
<td>( b (V) )</td>
<td>( c (V) )</td>
</tr>
<tr>
<td>((1.0188 \pm 0.0165) \times 10^1)</td>
<td>((-2.1993 \pm 0.0593) \times 10^1)</td>
<td>((2.5772 \pm 0.0709) \times 10^1)</td>
</tr>
<tr>
<td>( a (V) )</td>
<td>( b (V) )</td>
<td>( c (V) )</td>
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<td>((2.5772 \pm 0.0709) \times 10^1)</td>
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</tr>
<tr>
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<td>((-2.1993 \pm 0.0593) \times 10^1)</td>
<td>((2.5772 \pm 0.0709) \times 10^1)</td>
</tr>
<tr>
<td>( x_0 ), the standard deviation (V)</td>
<td>(9.7772 \times 10^{-4})</td>
<td>(4.9544 \times 10^{-4})</td>
</tr>
</tbody>
</table>

Figure 5. Comparison of the experimental OCP curve of the cobalt oxide electrode for a discharge process and the curves predicted by polynomial regression. Two different orders, \( m = 10 \) and 15, were used in Eq. 14, and 32-digit precision was used in polynomial regression.
One can imagine that round-off error is significant if lower digit precision is used in the regression, because a finite value in the OCP of the cobalt oxide electrode is determined by the relatively small difference between two groups of terms having a large magnitude. In contrast, only 12-digit precision is required in cubic spline regression to guarantee the accuracy. Therefore, the cubic spline regression method is numerically more tolerant than the polynomial model.

Figure 6 presents the comparison of the experimental curves of the carbon electrode and its predicted OCP curves by cubic spline regression. As observed in Fig. 6, similar to the cobalt oxide electrode, the experimental OCP curve of the carbon electrode obtained

![Figure 6](image)

**Figure 6.** Comparison of the experimental OCP curves of the carbon electrode and the curves predicted by cubic spline regression. 12-digit precision was used in the regression.

Table II. The 95% confidence intervals for all the parameters used in Eq. 2 to fit the OCP curve of the carbon electrode. 12-digit precision was used in the regression.

<table>
<thead>
<tr>
<th>k, the number of knots</th>
<th>Discharge process</th>
<th>Charge process</th>
</tr>
</thead>
<tbody>
<tr>
<td>x&lt;sub&gt;1&lt;/sub&gt;, the knot coordinate</td>
<td>x&lt;sub&gt;1&lt;/sub&gt; = (4.7423 ± 0.3329) x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>x&lt;sub&gt;1&lt;/sub&gt; = 5.0000 x 10&lt;sup&gt;-1&lt;/sup&gt; (fixed)</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;2&lt;/sub&gt; = (1.6833 ± 0.4582) x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>x&lt;sub&gt;2&lt;/sub&gt; = (4.3510 ± 0.1545) x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;3&lt;/sub&gt; = (7.8218 ± 0.2513) x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>x&lt;sub&gt;3&lt;/sub&gt; = (1.4804 ± 0.1857) x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;4&lt;/sub&gt; = (1.5397 ± 0.0512) x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>x&lt;sub&gt;4&lt;/sub&gt; = (9.1037 ± 0.4839) x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;5&lt;/sub&gt; = (5.9697 ± 0.1060) x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>x&lt;sub&gt;5&lt;/sub&gt; = (1.3432 ± 0.0749) x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

First interval

**D<sub>i</sub>, the dummy variable**

<table>
<thead>
<tr>
<th>a (V)</th>
<th>b (V)</th>
<th>c (V)</th>
<th>d (V)</th>
<th>e&lt;sub&gt;1&lt;/sub&gt; (V)</th>
<th>e&lt;sub&gt;2&lt;/sub&gt; (V)</th>
<th>e&lt;sub&gt;3&lt;/sub&gt; (V)</th>
<th>e&lt;sub&gt;4&lt;/sub&gt; (V)</th>
<th>e&lt;sub&gt;5&lt;/sub&gt; (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2623 ± 0.4862</td>
<td>-6.3949 ± 9.6734 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>-2.3261 ± 0.7979</td>
<td>1.2853 ± 0.4282</td>
<td>-3.7276 ± 0.4261</td>
<td>(1.4102 ± 1.5662) x 10&lt;sup&gt;1&lt;/sup&gt;</td>
<td>(-1.0475 ± 0.1351) x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>(-9.4697 ± 1.3514) x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

| SE<sub>e</sub>, the standard deviation | 1.6935 x 10<sup>-3</sup> | 1.9637 x 10<sup>-3</sup> |

| a<sub>i</sub> was fixed to a value in this work due to the difficulty in convergence. |
| b If x<sub>i</sub> values are fixed to the point estimates presented, the confidence intervals for a and e<sub>2</sub> are (-6.3949 ± 3.2232) x 10<sup>-2</sup> and (1.4102 ± 0.2151) x 10<sup>1</sup>, respectively. The confidence intervals for the other parameters are also made smaller than those presented. |
in a charge process differs from that obtained in a discharge process. These two OCP curves were also fitted separately in this work. One can also observe from Fig. 6 that each experimental curve exhibits three voltage plateaus and a spike. This agrees with the results mentioned before, we cannot simply conclude that these two parameters are statistically insignificant. In some cases, the uncertainty of a curve obtained in a discharge process. This indicates uncertainty in determining the first regression interval away from a steep portion of an OCP curve achieved at the cost of using 32-digit numerical precision, and an attempt to lower the precision to a smaller number, i.e., 16 digits, caused significant error in the regression.

**Conclusions**

The cubic spline regression model presented here is useful for fitting complicated profiles such as the experimental OCP curves of intercalation electrodes. Even though a few intervals need to be defined and the model equation has a form varying from one interval to another, the model predictions are smooth within the entire range of the experimental data points because the dependent variable, and its first and second derivatives, are all continuous within that range. Round-off error can be avoided in cubic spline regression by choosing the first regression interval away from a steep portion of an OCP curve.

In general, using a high-order polynomial equation to fit an OCP curve of an intercalation electrode is not recommended because such a fit does not provide the accuracy needed.

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**Appendix**

The discharge process of the cobalt oxide electrode

The exact form of Eq. 2 for the first regression interval, \( x_2 < x < x_1 \), is

\[
 y = a + bx + cx^2 + dx^3 \tag{A-1}
\]

The exact form of Eq. 2 for the second regression interval, \( x_1 < x < x_2 \), is

\[
 y = a + bx + cx^2 + dx^3 + e_1(x - x_1)^3 + e_2(x - x_1) \tag{A-2}
\]

The exact form of Eq. 2 for the third regression interval, \( x > x_2 \), is

\[
 y = a + bx + cx^2 + dx^3 + e_1(x - x_1)^3 + e_2(x - x_1) \tag{A-3}
\]

The exact form of Eq. 2 for the fourth regression interval, \( x_4 < x < x_3 \), is

\[
 y = a + bx + cx^2 + dx^3 + e_1(x - x_3)^3 + e_2(x - x_3) \tag{A-4}
\]

The exact form of Eq. 2 for the fifth regression interval, \( x_5 < x < x_4 \), is

\[
 y = a + bx + cx^2 + dx^3 + e_1(x - x_3)^3 + e_2(x - x_3) \tag{A-5}
\]

The exact form of Eq. 2 for the sixth regression interval, \( x < x_5 \), is

\[
 y = a + bx + cx^2 + dx^3 + e_1(x - x_3)^3 + e_2(x - x_3) + e_3(x - x_3) \tag{A-6}
\]

**List of Symbols**

- \( a \), \( b \), \( c \), \( d \), \( e_i \) fitting parameters (see Eq. 1 and 14), V
- \( a_k \) \( k \)th element of the diagonal of the matrix \( a = \{x_1 \times \times x_n\}^{-1} \)
- \( b \) fitting parameter (see Eq. 2-5, and A-1 through A-6), V
- \( b_{i} \) fitting parameter (see Eq. 1), V
- \( c_{i} \) fitting parameter (see Eq. 2-5, and A-1 through A-6), V
- \( d_{i} \) fitting parameter (see Eq. 1), V
- \( D_i \) dummy variable which takes a value of 1 or 0
- \( e_i \) fitting parameter (see Eq. 2), V
- \( J_i \) Jacobian matrix of the ith regression interval
- \( k \) number of knots
- \( m \) order of the polynomial equation, see Eq. 14

\( ^{*} \) See Fig. 2.
Greek:

θ vector of fitting parameters (a, b, c, d, e, and i), V
θi ith fitting parameter, V
θi* point estimate of the ith fitting parameter, V
Δθi vector of the incremental values of fitting parameters, V
Φ sum of squared residuals, V^2

Superscripts:

T transpose
−1 inverse

References: