Capacity Fade Analysis of Lithium-Ion Cells Utilizing Uncertainty Quantification Approach

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Abstract

Lithium-ion batteries (LIBs) have drawn attention in research due to their broad range of applications. To achieve low-cost and high-reliable batteries, researchers have worked on a variety of degradation phenomena. Among them, the Solid Electrolyte Interphase (SEI) layer is the most important degradation phenomenon and causes the cell to capacity fade and internal resistance raise. In this paper, a stochastic approach, based on the sparse Jacobi polynomial chaos expansion, is utilized to investigate the effect of the uncertainty sources on the lithium-ion battery aging. Furthermore, the importance of every uncertainty source is calculated by using Sobol indices. Capacity fade and resistance raise obtain at the end of the Constant Current-Constant Voltage (CC-CV) charging. The outcome of this study shows the most important parameters affecting capacity fade and voltage drop.

Keywords: Li-ion battery, Aging, Degradation, SEI, Uncertainty Quantification, Global Sensitivity Analysis

1. Introduction

Lithium-ion batteries not only have taken over the portable electronic devices market but also have conquered the electric car market [1]. To improve lithium-ion batteries performance, one of the major bottlenecks of LIBs is its aging [2]. As a result of an in-depth understanding of the degradation mechanisms in LIBs, longer lifespan and more cost-effective batteries can be produced. Therefore, electric cars having inexpensive batteries can compete in the car market. Although a great deal of research has made attempts to find out lithium-ion cell aging [3, 4], so complicated are the degradation processes that further research is still required to understand how much effect has the input parameters on the degradation. Mathematical modeling is a useful tool for investigating the degradation phenomena in detail, which sometimes cannot be acquired by the experimental studies. However, in the present study, a strong relationship between mathematical modeling and experiments is established, which helps quantify the amount of impact of each input parameter on the cell aging in LIBs.

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Early attempts to model the electrochemical processes and transport phenomena in the Li-Ion cell led to Pseudo Two Dimensional (P2D) model [5, 6], which is elicited from the concentrated solution and porous electrode theories. The P2D model provides the simulation of the cell with a robust framework, which can be used to capture aging phenomena [3].

Several degradation mechanisms occur in a lithium-ion cell, among which SEI has a considerable influence on the capacity fade [7]. Since the potential of the intercalation reaction on the negative electrode is less than the reduction reaction of the solvent at the electrode/electrolyte interface, a growing passive layer, as shown in Figure 1, is formed [8]. On the one hand, SEI, which is formed on a first cycle and grow during cycles, protects the electrode from corrosion and electrolyte from reduction. On the other hand, SEI formation reduces active lithium and increases internal resistance, and as a result, it is essential to understand the role of SEI in lithium-ion batteries [9]. The passive layer has been modeled with two cyclic and calendar approaches [10]. The calendar aging approach is utilized for storage, while the cyclic aging approach considers degradation during charge or discharge cycles. The former model illustrates the self-discharge process taking place in the lithium-ion cell [11]. Various methods have been employed for SEI modeling, either calendar or cyclic, such as polynomial expressions for the prediction of irreversible and reversible capacity fade [12], a semi-empirical approach for capacity loss estimation [13], the impacts of SEI growth on charge/discharge performance [14], solvent-diffusion model [15], kinetic-limited model [2], capacity fade during open-circuit voltage storage [16], a multimodal aging model [17], an extended multimodal aging model [18], and Mixed Mode Growth [19]. However, in this paper, the cyclic kinetic-limited model developed by Ramadass et al. [2], which is well consistent with the test results trend and can be used well with the P2D model, is utilized.

One of the most critical concerns for designing experiments is the uncertainty in the system, meaning that the same experiments in different laboratories have different results [20]. Deterministic simulations with the same input parameters have the same results, but the results of repeated experiments cannot be as same as one another [21]. Therefore, taking uncertainty quantification into account is also required for the validation of numerical simulations [22]. The lithium-ion cell degradation has a significant dependency on the determining of its effective parameters, yet most of the physical parameters affecting the performance of the cell and SEI growth cannot be accurately measured, and therefore a complete understanding of these impacts is not clear. In the recent researches, there are a few publications in the literature with a stochastic viewpoint [23, 24, 25, 26], and most of them considered the physical parameters of the cell to be deterministic. Polynomial chaos expansion was presented to show the effect of uncertainty in the particle radius in the negative electrode with Gaussian distribution on the cell voltage [23]. In order to estimate the specific energy and power in given cathode particle size, cycling rate, electrical conductivity, and diffusivity of a Li-Ion cell, a mixed model was proposed with the combination of the polynomial response, kriging and radial-basis neural networks [24]. That the electrical conductivity does not affect the cell voltage and that the particle size, diffusivity, and current density affect the available energy of the cell were elicited from the simulation of the mixed method [24]. So as to study the influences of uncertainties on Li-Ion cell capacity, voltage, and electrolyte concentration, a sampling technique is introduced using sparse polynomial chaos expansion. The most impactful parameters are also obtained,

utilizing sensitivity analysis [25]. The Jacobi polynomial chaos expansion was proposed to quantify a lithium-ion battery, and the coefficients of the expansion were calculated with Smolyak algorithm via non-nested Gauss-Jacobi. This approach provides not only an almost independent on the dimension of probability space but also fast convergence and high accuracy model [26]. In this paper, an attempt is made to address the gap in the literature, since there is not any study which quantifies uncertainties of aging in lithium-ion cells.

Mostly, the uncertain model parameters are indicated by random processes known as probabilistic approaches. In this case, classical methods, such as Monte Carlo sampling (MCS) [27] and perturbation-based methods [28], are not proper. MCS converges slowly, and perturbation-based methods are confined with the range of the parameters of interests. To not have mentioned restriction, the stochastic spectral method [28, 29] utilizing polynomial chaos (PC) expansion [30, 31] is considered by this study. Furthermore, the presented method has a fast convergence rate and considerable accuracy [27]. In this paper, the coefficients of PC-expansion are computed non-intrusively [32]. Unlike intrusive methods [28, 29], non-intrusive ones have less computational cost and can be easily implemented in complicated physics, such as electrochemical systems.

In this study, 32 parameters of a Li-Ion cell in different voltage charging are considered to quantify uncertainties on cell degradation. The Jacobi polynomial chaos expansion is used to evaluate the influences of input uncertainties on capacity fade and internal resistance raise of the lithium-ion batteries. In addition, a global sensitivity analysis is employed to identify the most crucial parameters producing the most uncertainties in the lithium-ion battery aging.

2. Mathematical Modeling

A lithium-ion cell consists of a positive current collector (Al), a positive electrode (LiMO_2), separator, a negative electrode (Li_xC_6), and a negative electrode current collector (Cu) as shown in the Figure 2. The electrodes as well as separator are filled with electrolyte. Having high conductivity, the current collectors pass the electric current. In other words, the distribution of the electric potential in these regions can be neglected. Only thickness is considered for mathematical modeling because the other dimensions are much larger than the thickness, and the gradients along the thickness are more significant than the other dimensions.

2.1. Electrochemical Reactions

During charging process lithium ions are intercalated as following half electrochemical reaction in the positive electrode:

After de-intercalating from the negative electrode, lithium ions migrate from the negative electrode through the electrolyte and separator to the positive electrode. Separator, which is electrical insulation, does not allow the electrons to move along the separator. Therefore, electrons move from an electrode to the another through the external circuit.

The process is shown in the half electrochemical reaction as:

SEI on the positive electrode is much thinner than that on the negative electrode, so SEI on the positive electrode is neglected. Considering ethylene carbonate EC as the organic solvent for the electrolyte, the most straightforward reaction for the capacity fade is the reduction of EC as follows [2].

2.2. Governing Equations

In this paper, the capacity fade model is coupled with the P2D lithium-ion cell model. The engaged unknowns are the electric potential in the solid and electrolyte ($\phi_s(x)$ and $\phi_e(x)$), concentration of Li ions in the electrolyte and solid particles ($C_e(x, t)$ and $C_s(r, t)$).

2.2.1. Solid Electrolyte Interphase model

The local molar flux j_{total} in the electrodes is given by a sum of the intercalation flux, j_{int} , and the side reaction flux, j_s , as follows,

$$j_{total} = j_{int} + j_s \quad (4)$$

where j_{int} is obtained with the Butler—Volmer electrochemical kinetic equation,

$$j_{int} = k_i(C_{s,max,i} - x_{s,surf,i}C_{s,max,i})^{1-\alpha}(x_{s,surf,i}C_{s,max,i})^\alpha C_{e,i}^{1-\alpha} \left\{ \exp\left(\frac{(1-\alpha)F}{RT}\eta_i\right) - \exp\left(-\frac{\alpha F}{RT}\eta_i\right) \right\} \quad (5)$$

where J_{int} is the pore wall flux, $x_{s,surf,i}$ is state of charge (SoC) of each electrodes ($x_{s,surf,i} = \frac{C_{s,i}}{C_{s,max,i}}$), and η is over potential $\eta_i = \phi_{s,i} - \phi_{e,i} - U_i(x_{s,surf,i}) - FR_{film}j_{total}$

Due to irreversibility of the side reaction, a Tafel equation is utilized to describe the kinetics of the side reaction in the negative electrode,

$$j_s = -\frac{i_{0,s}}{F} \left\{ \exp\left(-\frac{\alpha_s F}{RT}\eta_s\right) \right\} \quad (6)$$

where η_s is over potential $\eta_s = \phi_s - \phi_e - U(x_{s,surf}) - FR_{film}j_{total}$. In the positive electrode j_s is considered to be zero.

The change in the film thickness can be computed by,

$$\frac{\partial \delta_{film}}{\partial t} = -\frac{M_p}{\rho_p} j_s \quad (7)$$

where ρ_p is the average density and M_p is the average molecular weight of the constituent compounds of the SEI layer.

Film resistance is calculated as,

$$R_{film} = R_{film,0} + \frac{\delta_{film}}{\kappa_p} \quad (8)$$

Finally the capacity loss is calculated as,

$$\frac{\partial Q}{\partial t} = \int_0^{L_n} a_n A F j_s dx \quad (9)$$

The aging model described in this section is presented in [2] in detail.

2.2.2. Electrical Potential in each Electrode

Ohm's law is used to model potential in solid as follows,

$$\frac{\partial}{\partial x} \left(\sigma_{\text{eff},i} \frac{\partial \phi_{s,i}}{\partial x} \right) = a_i F j_{\text{total}}, \quad (10)$$

At the current collector/electrode interface, relying on the type of charging process (constant current or voltage) the boundary conditions are modeled as below,

$$-\sigma_{\text{eff},i} \frac{\partial \phi_{s,i}}{\partial x} \Big|_{x=0,L} = I_{\text{app}} \quad (\text{constant current}) \quad (11a)$$

$$\phi_p|_{x=0} = 0, \quad \phi_n|_{x=L} = V \quad (\text{constant voltage}) \quad (11b)$$

Because the boundaries are electrically insulated, the electric current flux at the electrode/electrolyte interface is zero.

$$\frac{\partial \phi_{s,p}}{\partial x} \Big|_{x=L_p} = 0, \quad \frac{\partial \phi_{s,n}}{\partial x} \Big|_{x=L_p+L_s} = 0. \quad (12)$$

2.2.3. Electrolyte Potential in the Electrolyte

In order to model the electric potential in the electrolyte, in addition to the Ohm's law, Li-ions diffusion in the electrolyte must also be considered as follows,

$$\frac{\partial}{\partial x} \left\{ \kappa_{\text{eff},i} \left[\frac{\partial \phi_{e,i}}{\partial x} + k_{\text{junc}} \frac{\partial \ln C_{e,i}}{\partial x} \right] \right\} = -\zeta a_i F j_{\text{total}}, \quad \begin{cases} \zeta = 1, & i = p, n \\ \zeta = 0, & i = \text{sep} \end{cases} \quad (13)$$

where liquid-junction potential k_{junc} and thermodynamic factor ν are given by,

$$k_{\text{junc}} = \frac{2RT}{F} \nu. \quad (14)$$

$$\nu = - \left[1 + \frac{\partial \ln f}{\partial \ln C_{e,i}} \right] (1 - t_+^0) \quad (15)$$

where R refers to the universal gas constant, F is the Faraday's constant, T refers to temperature, and f is the activity coefficient of salt in the electrolyte, which is considered to be one, and t_+^0 is the transference number of lithium ion relative to the solvent.

The lithium ions move neither out nor in the current collector/electrode boundary, so the electric charge flux carried by the ions is zero at the boundaries,

$$\frac{\partial \phi_e}{\partial x} \Big|_{x=0} = 0, \quad \frac{\partial \phi_e}{\partial x} \Big|_{x=L_n} = 0. \quad (16)$$

2.2.4. Electrolyte Concentration

The conservation of chemical species equation for Li-ion in the electrolyte is derived with concentrated solution theory where with some simplifications can be written as follows [33],

$$\frac{\partial C_e}{\partial t} = \frac{1}{\varepsilon_i} \frac{\partial}{\partial x} \left(D_{e,i} \frac{\partial C_{e,i}}{\partial x} \right) + \zeta \frac{(1 - t_+^0) a_i j_{\text{total}}}{\varepsilon_i}, \quad \begin{cases} \zeta = 1, & i = p, n \\ \zeta = 0, & i = \text{sep} \end{cases} \quad (17)$$

115 where D_e and t_+^0 are the diffusion coefficient and the transference number, respectively. Chemical species flux cannot
 116 enter either in or out of the the current collector/electrode interface boundaries.

$$\left. \frac{\partial C_i}{\partial x} \right|_{x=0,L} = 0, \quad i = p, n. \quad (18)$$

117 As a result of a long rest before starting the simulation, the initial condition of the Li-ions concentration in the
 118 electrolyte is assumed to be constant.

$$C_{e,i} = C_{e,i,0} \quad t = 0 \quad (19)$$

119 2.2.5. Solid Concentration

120 The Fick's second law models Li-ions diffused into solid particles, as the following equation,

$$\frac{\partial C_{s,i}}{\partial t} = \frac{D_{s,i}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{s,i}}{\partial r} \right), \quad i = p, n. \quad (20)$$

121 The flux of lithium-ions either produced or consumed is limited with the rate of the electrochemical reaction as
 122 below [33],

$$-D_{s,i} \left. \frac{\partial C_{s,i}}{\partial r} \right|_{r=R_i} = j_{int} \quad i = p, n. \quad (21)$$

123 At the center of the particle, the concentration flux is considered to be zero as follows,

$$\left. \frac{\partial C_{s,i}}{\partial r} \right|_{r=0} = 0 \quad (22)$$

124 The initial condition for the concentration of lithium in the spherical particles is determined with the initial state of
 125 charge.

$$C_{s,i} = x_{s,surf,i} C_{s,max,i} \quad t = 0 \quad (23)$$

126 3. Numerical Simulation

127 In this study, the governing equations of the lithium-ion cell and SEI growth are discretized by the finite-volume
 128 method (ECM-CVM [34, 35]) and implemented in an object-oriented C++ code to simulate the aging of the cell
 129 deterministically. Results from the code are utilized as the sampling data for the uncertainty quantification study. The
 130 P2D model partial differential equations seem quite stiff and nonlinear, so the number of deterministic simulation
 131 required in UQ study exponentially boosts if more inputs are considered stochastically. To reduce the computational
 132 cost and make the simulation possible, an efficient method must be used to solve PDEs, especially when it comes to
 133 aging. Combinations of ECM [35] and either CVM [34] or CPI [35] methods become fast enough to allow a great
 134 deal of simulation which is demanded for UQ analysis. Moreover, only 2177 samples of deterministic results are
 135 demanded for each case due to using the sparse grid. Therefore, Considering 50 charges taking a total of 108850
 136 charges for each result. This simulation is possible due to the use of fast methods for both battery and UQ code.

4. Parameters of a lithium-ion cell with Uncertainty

As a result of experimental and manufacturing errors, the battery model parameters are uncertain. UQ provides the Li-ion cell aging study with a robust framework for investigating the uncertainty in the parameters and their impact. The results guide manufacturers and researchers to pay more attention to which parameters and in which part of the production so that they can design new cells to slow down capacity loss and voltage drop. the appropriate measurement methods of considered 32 parameters along with their probability distribution are discussed.

4.1. Electrical conductivity of electrode (σ)

Electrical conductivity of electrode could be measured using two-point or four-point probes techniques [36]. As enough information about the uncertainty of this parameter is not available, the probability distribution of the parameter is considered beta distribution ($\alpha = 5$ and $\beta = 5$) with $\pm 10\%$ around the nominal value of the parameter [37].

4.2. Electrical conductivity of electrolyte (κ)

The electrolyte is composed of a multi-component system. Due to the concentrated solution theory, ten independent transport properties are needed for the mixture to describe the transport processes in the electrolyte. Little information is available because of not developing experimental methodologies, so there is no complete description of the electrolyte properties. The electrolyte conductivity is obtained by fitting a function of temperature and concentration of Li-ions in the electrolyte through experiments [38]. As a consequence of measurements and manufacturing errors, the uncertainty in the electrolyte conductivity is applied by multiplying a random parameter (ζ_κ) with the probability distribution of ($\alpha = 5$ and $\beta = 5$) beta distribution with $\pm 1.5\%$ around unit.

4.3. Diffusion coefficient of electrode (D_s)

Intercalation flux is affected by solid diffusion coefficient. Electrochemical procedures have been utilized to determine D_s , such as CV, GITT, and EIS [39]. D_s depends on the Li concentration in the particles [40], but D_s has been frequently considered as a constant [6]. So as to considering D_s independently of Li concentration in particles, the beta distribution for D_s is taken into account ($\alpha = 5$ and $\beta = 5$) with $\pm 10\%$ around the nominal value of the parameter.

4.4. Diffusion coefficient of electrolyte (D_e)

The electrolyte diffusion coefficient D_e is a measure of the friction forces between the ions and the solvents [41]. The higher charge rate applies to the cell, the more concentration gradient is in the electrolyte, and the more important is the role of electrolyte diffusion. To measure D_e , Experimental methods have been utilized, such as cyclic voltammetry (CV) [42] and electrochemical impedance spectroscopy (EIS) [43]. Although experiments were shown that D_e depends on Li-ions concentration and temperature [44], it is considered constant with the beta distribution ($\alpha = 5$ and $\beta = 5$) with $\pm 10\%$ around the nominal value of the parameter.

4.5. Thermodynamic factor (v)

The thermodynamic factor was expressed as a function of concentration for several temperatures approximately [44]. Besides, the simulation performed in this work is at a different temperature rather than the test conditions. Therefore, the parameter is considered uncertain with the mean value of $(1 - t_+^0)$ with $\pm 1.5\%$ around the nominal value of the parameter.

4.6. Bruggeman coefficient (ex)

Since the simulation of a cell utilizing micro-scale models is not feasible, macro-scale models capturing dominant physics is used. Accordingly, P2D model creates a macro-scale model using volume averaging method over a small and finite unit of volume [45]. Although the length scale is greater than the particles' radius, P2D is highly accurate. The characteristic length of the averaging volume is far larger than the openings between particles and far less than the electrode length. In this regard, effective properties, such as κ_{eff} , β_{eff} , σ_{eff} , and $D_{eff,e}$, is used instead of bulk properties. The effective transport properties are obtained utilizing the constrictivity ($\delta < 1$), porosity (ϵ), and tortuosity ($\tau > 1$) via

$$\sigma_{eff} = \epsilon \frac{\delta}{\tau} \sigma \quad \kappa_{eff} = \epsilon \frac{\delta}{\tau} \kappa \quad D_{eff,e} = \epsilon \frac{\delta}{\tau} D_e \quad (24)$$

By considering ϵ^{ex} equals to $\epsilon \frac{\delta}{\tau}$, the Bruggeman coefficient is chosen so that the averaging volume method can correspond to the macroscale. Based on the reports in [46, 59], $\pm 5\%$ variations around the mean value in the electrodes and $\pm 20\%$ in the separator is considered.

4.7. Transference number (t_+^0)

The portion of ionic current which is carried by a specific ion in the absence of gradient in chemical potential is called a transference number. In a Lithium-ion cell, LiPF_6 is decomposed into Li^+ and PF_6^- , so the transference number of Li^+ is considered. Regularly, the parameter is measured by Hittorf's method [48], such as AC impedance spectroscopy [49] and pulsed-field gradient for obtaining nuclear magnetic resonance (PFG-NMR) technique [50]. PFG-NMR technique has $\pm 5\%$ error [44], and consequently, t_+^0 is considered $\pm 5\%$ around mean value with the beta distribution ($\alpha = 5$ and $\beta = 5$).

4.8. Open circuit potential (U)

Although open circuit potential is a function of solid concentration at the electrode/electrolyte interface, it is considered as a function of SOC due to neglecting variation of density. The SEI layer that exists at the electrode/electrolyte interface is not explicitly accounted for obtaining open circuit potential [51]. For the positive electrode, C/60 rate was applied after completing the formation of SEI to obtain open circuit potential [52]. On the one hand, the test conditions were at low rates rather than zero rate, and the results were not completely accurate, on the other hand, due to the lack of information the exact error cannot be stated. However, a random coefficient with $\pm 1.5\%$ around mean value with the beta distribution ($\alpha = 5$ and $\beta = 5$) is multiplied to the open circuit potential function to convert it to a random process.

4.9. Reaction rate constant (k)

That the exchange-current density is calculated at the initial state lets calculation of the reaction rate constant k_i with this relation $i_0 = k_i(C_{s,\max,i} - x_{s,\text{surf},i}C_{s,\max,i})^{1-\alpha}(x_{s,\text{surf},i}C_{s,\max,i})^\alpha C_{e,i}^{1-\alpha}$ by having initial conditions for concentrations [53]. The reaction rate constant depends on temperature and the electrode surface [54], but it is considered as a constant for simulation of lithium-ion cells. Due to the lack of data for the parameter, it is assumed $\pm 10\%$ around mean value with the beta distribution ($\alpha = 5$ and $\beta = 5$).

4.10. Solid Electrolyte Interphase input parameters

The deposition has several parameters that are all considered in this study, such as electrical conductivity (κ_{SEI}), exchange current density ($i_{0,s}$), charge-transfer coefficient (α_s), molecular weight (M_{SEI}), and density (ρ_{SEI}).

Although SEI is conductive with respect to Li-ions, it is insulating regarding electrons [55]. In this model, electrical conductivity is assumed to be unlimited for Li-ions and a limited amount for electron. Since there is not any measurement of the SEI conductivity [56], the probability distribution of the parameter is assumed beta distribution ($\alpha = 5$ and $\beta = 5$) with $\pm 10\%$ around the nominal value of the parameter. The exchange current density is vary depending on the reaction rate constant, the concentration of the reactants, and the products. There are models considering either the diffusion of solvent [17] or electron [57, 58] in the SEI to obtain the exchange-current density. Although this parameter is assumed to be constant in this study, being stochastic reflects the mentioned changes.

4.11. Porosity (ϵ)

The porosity is the volume fraction of the total volume. Method of Standard Porosimetry (MSP) [59], porosity measurement using liquid or gas absorption methods [60], and X-ray [61] are utilized to measure porosity. Based on experimental data for the porosity of LiCoO_2 , $\pm 6.7\%$ variation around the mean value was reported [46]. $\pm 4.5\%$ and $\pm 12.6\%$ variation around the mean value was considered by [59] for porosity of the negative electrode and separator. The same variations are considered in this study.

4.12. Geometry (L and A)

The thickness of regions of the cell and geometric surface area of the electrode is considered as a parameter with uncertainty to take into account manufacturing errors [46, 25].

4.13. Radius (r)

The available surface area for the electrochemical reaction, related to the radius, affects the Li-ions flux at the interface. In this regard, the distribution of the particle size is measured by either scattering device with laser diffraction [62], X-ray tomography [63], or ion beam tomography [64]. Normal distribution for the negative electrode with a mean of 6.2 mm and a standard deviation of 0.42 mm was reported [23]. For the positive electrode, a normal distribution with the mean and standard deviation of 7.7 mm and 1.5 mm was considered [25]. In this study, a beta

distribution with the variations, capturing 99.99% data of the normal distribution in the literature, around mean value with the beta distribution ($\alpha = 5$ and $\beta = 5$) is selected.

4.14. Constant charging voltage (V)

Different chargers are produced by various companies. According to the datasheet provided by the manufacturers, the constant-voltage charging error ranges from $\pm 0.5\%$ to $\pm 5\%$. Nevertheless, $\pm 1\%$ error is considered in this study.

5. Results and Discussions

In this paper, Gauss-Jacobi abscissas is used with the Jacobi polynomial chaos (PC) expansion on a sparse grid constructed by the Smolyak algorithm. For 32 input parameters, 2177 deterministic simulations of the LiB cell are performed to evaluate the coefficients of PC expansion with level parameter of two.

The variations of cell capacity (Q) as a function of cycles are shown in Figures 3a, 4a, 5a and 6a for 1C 4.2V, 1C 4.1V, 1C 4.0V, and 4C 4.2V of CC-CV charging, respectively. The sensitivity analysis of the cell capacity is utilized, presented in Figures 3b, 4b, 5b and 6b, for evaluating the importance of uncertain parameters on the capacity fade. The variation of resistance raise is also shown in Figures 7a, 8a, 9a and 10a and Sobol indexes are presented in Figures 7b, 8b, 9b and 10b. Results show that the uncertainties lead the capacity fade and resistance raise to change with respect to the deterministic simulation output. Uncertain parameters with Sobol indexes of $\max(S_k) < 0.01$ are considered less important, so they are not shown. The importance of the uncertain parameters is explained below.

5.1. Open circuit potential in positive electrode (U_p)

That Li-ions move to which direction depends on whether the potential difference between the electrode and the electrolyte is less than open circuit potential or not. Due to the materials' impurities, different cells may have different open circuit potential. Also, the method which is used to evaluate open circuit potential can be a source of uncertainties. While U_p has the highest impact on the capacity fade, U_n has little impact based on Figure 3b. On the one hand, the higher measurement accuracy of U_p leads to a more accurate estimation of the battery life and the number of cycles a battery can operate, on the other hand, the measurement accuracy of the U_n is not required to exactly predict capacity fade. Besides, Figures 3b, 4b, 5b and 6b reveal that the impact of open circuit potential depends on EOCV and is not dependent on C-rate, meaning that the less EOCV, the more important the role of open circuit potential. Like capacity fade, the open circuit potential in the negative electrode is not an important parameter for resistance raise based on Figure 7b. The open circuit potential in the positive electrode for resistance raise is a very effective parameter, but not as much important as for capacity fade.

5.2. End of charge voltage (EOCV)

Not only does EOCV affect the maximum capacity of the cell, but also it is the second most important factor affecting the capacity fade based on Figure 3b. Having more accurate chargers gives the customer a better estimation

of the end of the battery life. Battery manufacturers should also announce the accuracy of the charger to make sure their estimation of the battery life is reliable for costumers. The charging rate does not change the significant of EOCV, but the value of EOCV is effective in the importance of EOCV itself. Figures 3b, 4b, 5b and 6b show that the less is the value of the EOCV, the higher is the effect of the EOCV on the capacity fade of the cell. Figure 7b reveals that EOCV also affects the voltage drop, but its impact is far less than its effect on capacity reduction. Nevertheless, using more precision chargers allows the customer to trust in the battery datasheet.

5.3. Geometry of the cell and particle radius

Figures 3b, 4b, 5b and 6b reveal that in the first few cycles, the radius of negative electrode particles does not affect the capacity fade, but after a few cycles, it rapidly illustrates its effect on the capacity fade. Changing C-rate and EOCV have no considerable impact on the capacity fade, considering the amount of uncertainty impact of the radius value of the negative electrode on the capacity fade. The length of the positive electrode is initially more effective on the capacity fade, but its effect is reduced. Cell area is one of the most effective parameters in the capacity fade. The effect of positive electrode length and area decrease with decreasing EOCV. However, with the change in the C-rate charging, the influence of the input parameters is almost negligible. Radius at the positive electrode, length of the negative electrode, and length of the separator do not affect capacity fade. As a result, in the process of lithium-ion cell manufacturing, particles of the negative electrode, length of the positive electrode, and area should be accurately produced at the optimum point to delay capacity fade during the working cycles of a lithium-ion cell. On the other hand, investment for high-precision production for positive electrode particles and negative electrode length is not worth considering. Unlike capacity fade, the area does not affect the power drop. The radius of the negative electrode and length of the positive electrode also have a significant effect on the voltage drop. The length of the negative electrode has also impact on resistance raise. Separator thickness affects neither the capacity fade nor the resistance raise.

5.4. Porosity

Porosity involves directly in the P2D model of lithium-ion cells and the calculation of effective properties of the porous electrodes. Therefore, it seems that the porosity plays a crucial role in cell performance based on mathematical viewpoint. As it can be seen in Figures 7b, 8b, 9b and 10b, results of the uncertainty quantification study also indicate that the porosity of the positive electrode is the most important parameter of the lithium-ion battery affecting the voltage drop. In addition, the porosity of the positive electrode affects capacity fade, but it is not the most important input parameter. However, as shown in Figures 3b, 4b, 5b and 6b, the porosity of the negative electrode influences voltage drop, not capacity fade. These results indicate that manufacturers should pay more attention to the positive electrode porosity to achieve a higher number of operating cycles for LIBs.

6. Conclusion

In this study, the Jacobi polynomial chaos expansion is employed to quantify capacity fade and resistance raise of a lithium-ion cell as well as the global sensitivity analysis via Sobol indexes which is used to calculate the most effective parameters on the capacity fade and resistance raise under different current and voltage charging conditions. In this paper, 32 parameters of a lithium-ion cell are considered quantifying the uncertainties to manufacture optimum cell to decrease degradation. Manufacturing process can be remained at the optimum point by reducing the effect of uncertainties. performance, so it is required to control uncertainties for manufacturing reproducible products. This study creates a framework that lets researchers know which parameters should be focussed for research, which helps improve the manufacturing process, leading to the reproducibility of battery production. In addition, the manufacturers can be aware that which parameters need more attention to gain better cycle life with less cost. Although, the particle radius distribution of each electrode is considered to be uniform in this study, the particle radius distribution is not uniform across the electrodes. Considering the uncertainty effects for the radius of each particle on the performance of a lithium-ion cell will be the subject of future research.

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427 Appendix A. Polynomial Chaos Expansion

428 The solution of a stochastic process, in PC expansion framework, is projected onto bases of polynomials of the
429 random inputs, shown as bellow.

430 Let (Ω, Σ, P) be a probability space. The sample space is Ω , and P is a probability measure on the sigma-field Σ .
431 The output of interest is $\mathbb{R}$ -valued stochastic process U on (Ω, Σ, P) , and the uncertain inputs as a set of independent
432 random variables which is denoted by $\omega = (\omega_1, \dots, \omega_N)$ with probability density function, displayed as follows,

$$p_\omega(\omega) = \prod_{k=1}^N p_k^{(\alpha_k, \beta_k)}(\omega_k) \quad (25)$$

433 where p_ω is the joint probability density function of ω , and $p_k^{(\alpha_k, \beta_k)}$ is probability density function of ω_k , and $\alpha_k, \beta_k > 0$
434 are shape parameters. For stochastic process U , the finite o -th order Jacobi polynomial chaos expansion is as below,

$$\hat{U}(t, \omega) = \sum_{i \in \Gamma_{N,o}} \gamma_i(t) \psi_i(\omega) \quad (26)$$

435 where $\Gamma_{N,o}$ is set of multi-indices $i = \{i_1, \dots, i_N\}$ which is given by,

$$\Gamma_{N,o} = \left\{ i = \{i_1, \dots, i_N\} : \sum_{k=1}^N |i_k| \leq o \right\} \quad (27)$$

436 and $\psi_i(\omega)$ are multivariate basis functions, produced by multiplying Jacobi polynomials.

$$\psi_i(\omega) = \prod_{k=1}^d \psi_{i_k}(\omega_k) \quad (28)$$

437 Additionally, $\psi_{i_k}(\omega_k)$ are orthogonal polynomials respect to beta weights $p_k(\omega_k)$ with degree $i_k \in \mathbb{N}_0 = \mathbb{N} \cup \{0\}$,

$$E[\psi_{i_k} \psi_{j_k}] = \int \psi_{i_k}(\omega_k) \psi_{j_k}(\omega_k) p_k^{(\alpha_k, \beta_k)}(\omega_k) d\omega_k = \delta_{i_k j_k} E[\psi_{i_k}^2] \quad (29)$$

438 where $\delta_{i_k j_k}$ is the Kronecker delta, and $E[.]$ is the mathematical expectation operator.

439 The number of terms in the finite o -th order expansion is given by,

$$|\Gamma_{N,o}| = \frac{(N+o)!}{N!o!}. \quad (30)$$

440 According to independency of the input random variables ω_k , and orthogonality of Jacobi polynomials $\psi_{j_k}(\omega_k)$,
441 basis functions $\psi_i(\omega)$ are orthogonal. Therefore, the coefficients of Jacobi PC expansion are evaluated by,

$$\gamma_i(t) = E[U(t, \cdot) \psi_i(\cdot)] / E[\psi_i^2]. \quad (31)$$

442 After calculation of the PC coefficients, mathematical expectation $E[.]$ and variance $var[.]$ of the random output
443 of interest can be directly evaluated because of the orthogonality of PC basis,

$$E[U] = \gamma_0(t), \quad \tau_U^2 = var[U] = \sum_{i \neq 0} \gamma_i(t)^2 E[\psi_i^2] \quad (32)$$

444 where τ_U is the standard deviation of the output, gained by stochastic process. More details about Jacobi polynomial
445 chaos expansion can be found in [27, 29].

446 **Appendix B. Global sensitivity analysis**

447 After computation of the PC coefficients in Eq. (31), the total PC-based Sobol' indices as defined by,

$$S_k = \sum_{i \in \nu_k} \frac{\gamma_i(t)^2 \mathbb{E}[\psi_i^2]}{\text{var}[U]}, \quad \nu_k = \{i \in \mathbb{N}_0^N; i_k > 0\}. \quad (33)$$

448 The Sobol' indices are used to quantify the total influences of the random input ω_k , including the interactions between
449 random inputs on the variability of U. For the cases $S_k \ll 1$, ω_k is regarded as negligible random inputs on the
450 variability of U [65].

Nomenclature

a_i	specific interfacial area (m^{-1})
C	concentration (mol m^{-3})
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
F	Faraday's constant 96487 (C mol^{-1})
j_{int}	pore wall flux for intercalation ($\text{mol m}^{-2} \text{s}^{-1}$)
j_s	pore wall flux for side reaction ($\text{mol m}^{-2} \text{s}^{-1}$)
I	applied current (A cm^{-2})
L	thickness of cell component (m)
r	radial coordinate
M	molecular weight (kg mol^{-1})
Q	capacity of the electrode (A h)
R_{film}	resistance at the electrode/electrolyte interface (Ωm^2)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
t	time (s)
t_+^0	transference number of Li ions in electrolyte
T	temperature (K)
U_i	open circuit potential (V)
x	spatial coordinate
$x_{s,surf,i}$	dimensionless solid surface concentration (SoC)

Greek letters

α	transfer coefficients of electrochemical reaction
$\kappa_{e,i}$	electrolyte specific conductivity (S m^{-1})
κ_i	reaction rate constant ($\text{m}^{2.5} \text{mol}^{-0.5} \text{s}^{-1}$)
σ	effective solid conductivity (S m^{-1})
η_i	electrode overpotential (V)
ϕ_i	potential (V)
ϵ	volume fraction
ρ_i	density (kg m^{-3})
δ	film thickness (m)

Nomenclature (cont.)*Subscripts and superscripts*

eff	effective, corrected for tortuosity
e	electrolyte phase
max/min	maximum/minimum
p/n	positive/negative
app	applied
sep	separator
P	product formed because of side reaction

Table Captions

- Table 1 Expressions used in the governing equations of the lithium-ion cell
- Table 2 The uncertain parameters of the lithium-ion battery used in this study

Figure Captions

- Figure 1 Although the primary electrochemical reaction is the intercalation of lithium, lithium also reacts with components of the electrolyte to produce SEI [66].
- Figure 2 Governing equations of a lithium-ion cell along with the Schematic of the cell.
- Figure 3 Capacity fade at 1 C-rate, 4.2 V CC/CV charging
- Figure 4 Capacity fade at 1 C-rate, 4.1 V CC/CV charging
- Figure 5 Capacity fade at 1 C-rate, 4.0 V CC/CV charging
- Figure 6 Capacity fade at 4 C-rate, 4.2 V CC/CV charging
- Figure 7 Film resistance at 1 C-rate, 4.2 V CC/CV charging
- Figure 8 Film resistance at 1 C-rate, 4.1 V CC/CV charging
- Figure 9 Film resistance at 1 C-rate, 4.0 V CC/CV charging
- Figure 10 Film resistance at 4 C-rate, 4.2 V CC/CV charging

Table 1: Expressions used in the governing equations of the lithium-ion cell

Expressions	
Negative electrode open circuit potential	$U_n^{ref} = 0.72220.1387x_n + 0.029\sqrt{x_n} - \frac{0.0172}{x_n} + \frac{0.0019}{x_n^{1.5}} + 0.2808 \exp(0.9 - 15x_n) - 0.7984 \exp(0.4465x_n - 0.4108)$
Positive electrode open circuit potential	$U_p^{ref} = \frac{-4.656 + 88669x_p^2 - 401.119x_p^4 + 342.909x_p^6 - 462.471x_p^8 + 433.434x_p^{10}}{-1 + 18.933x_p^2 - 79.532x_p^4 + 37311x_p^6 - 73.083x_p^8 + 95.96x_p^{10}}$
The electrolyte conductivity	$\kappa = 4.1253 * 10^{-4} + 5.007 * c_e - 4.7212 * 10^3 * c_e^2 + 1.5094 * 10^6 * c_e^3 - 1.6018 * 10^8 * c_e^4$
Data from ref [2]	

Table 2: The uncertain parameters of the lithium-ion battery used in this study

The uncertain parameters of lithium-ion battery			
Parameter	Nominal Value	Distribution	Variation range
σ_p	100	Beta, $\alpha = 5, \beta = 5$	[90 _ 110]
σ_n	100	Beta, $\alpha = 5, \beta = 5$	[90 _ 110]
ζ_κ	1	Beta, $\alpha = 5, \beta = 5$	[0.985 _ 1.015]
κ_{SEI}	$1 * 10^{-6}$	Beta, $\alpha = 5, \beta = 5$	$[0.9 _ 1.1] * 10^{-6}$
$D_{s,p}$	$1 * 10^{-14}$	Beta, $\alpha = 5, \beta = 5$	$[0.9 _ 1.1] * 10^{-14}$
$D_{s,n}$	$3.9 * 10^{-14}$	Beta, $\alpha = 5, \beta = 5$	$[3.51 _ 4.29] * 10^{-14}$
D_e	$7.5 * 10^{-10}$	Beta, $\alpha = 5, \beta = 5$	$[6.75 _ 8.25] * 10^{-10}$
$c_{e,0}$	1000	Beta, $\alpha = 5, \beta = 5$	[900 _ 1100]
ζ_v	1	Beta, $\alpha = 5, \beta = 5$	[0.985 _ 1.015]
$ex_{e,p}$	4	Uniform	[3.8 _ 4.2]
$ex_{e,sep}$	4	Uniform	[3.2 _ 4.8]
$ex_{e,n}$	4	Uniform	[3.8 _ 4.2]
t_+^0	0.363	Beta, $\alpha = 5, \beta = 5$	[0.345 _ 0.381]
ζ_U	1	Beta, $\alpha = 5, \beta = 5$	[0.985 _ 1.015]
ζ_U	1	Beta, $\alpha = 5, \beta = 5$	[0.985 _ 1.015]
U_s	0.4	Uniform	[0.396 _ 0.406]
$k_{0,p}$	$2.334 * 10^{-11}$	Beta, $\alpha = 5, \beta = 5$	$[2.1 _ 2.56] * 10^{-11}$
$k_{0,n}$	$5.03 * 10^{-11}$	Beta, $\alpha = 5, \beta = 5$	$[4.52 _ 5.53] * 10^{-11}$
$i_{0,s}$	$1.555 * 10^{-11}$	Uniform	$[1.399 _ 1.710] * 10^{-11}$
α_s	0.5	Uniform	[0.4925 _ 0.5075]
ε_p	0.385	Beta, $\alpha = 5, \beta = 5$	[0.36 _ 0.41]
ε_{sep}	0.724	Beta, $\alpha = 5, \beta = 5$	[0.63 _ 0.81]
ε_n	0.485	Beta, $\alpha = 5, \beta = 5$	[0.46 _ 0.51]
M_{SEI}	0.13	Beta, $\alpha = 5, \beta = 5$	[0.117 _ 0.143]
ρ_{SEI}	2100	Beta, $\alpha = 5, \beta = 5$	[1890 _ 2310]
A	0.06046	Beta, $\alpha = 5, \beta = 5$	[0.05744 _ 0.06348]
L_p	80	Beta, $\alpha = 5, \beta = 5$	[77 _ 83]
L_{sep}	25	Beta, $\alpha = 5, \beta = 5$	[22 _ 28]
L_n	88	Beta, $\alpha = 5, \beta = 5$	[85 _ 91]
r_p	2	Beta, $\alpha = 5, \beta = 5$	[1.25 _ 2.75]
r_n	2	Beta, $\alpha = 5, \beta = 5$	[1.55 _ 2.45]
V	4.2	Beta, $\alpha = 5, \beta = 5$	[4.158 _ 4.242]
V	4.1	Beta, $\alpha = 5, \beta = 5$	[4.059 _ 4.141]
V	4.0	Beta, $\alpha = 5, \beta = 5$	[3.96 _ 4.040]

Data from ref [2]

Figure 1

Fig. 1: Although the primary electrochemical reaction is the intercalation of lithium, lithium also reacts with components of the electrolyte to produce SEI [66].

Figure 2

Fig. 2: Governing equations of a lithium-ion cell along with the Schematic of the cell.

Figure 3

Fig. 3: Capacity fade at 1 C-rate, 4.2 V CC/CV charging

Figure 4

Fig. 4: Capacity fade at 1 C-rate, 4.1 V CC/CV charging

Figure 5

Fig. 5: Capacity fade at 1 C-rate, 4.0 V CC/CV charging

Figure 6

Fig. 6: Capacity fade at 4 C-rate, 4.2 V CC/CV charging

Figure 7

(a) Mean value, variations and deterministic simulation

(b) Global sensitivity analysis

Fig. 7: Film resistance at 1 C-rate, 4.2 V CC/CV charging

Figure 8

(a) Mean value and variations around mean value

(b) Global sensitivity analysis

Fig. 8: Film resistance at 1 C-rate, 4.1 V CC/CV charging

Figure 9

(a) Mean value and variations around mean value

(b) Global sensitivity analysis

Fig. 9: Film resistance at 1 C-rate, 4.0 V CC/CV charging

Figure 10

(a) Mean value and variations around mean value

(b) Global sensitivity analysis

Fig. 10: Film resistance at 4 C-rate, 4.2 V CC/CV charging