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Block-oriented system identification for nonlinear modeling of All-solid-state Li-ion battery technology

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Abstract-The high energy density characteristic of the all-solid-state battery technology makes it one of the promising competitors of current liquid electrolyte-based lithium-ion batteries. However, due to low ionic conductivity of solid materials and existing issues in active material-solid electrolyte interfaces, all-solid-state batteries show strong nonlinear behavior when amplitude of input current in relatively high. In this paper, we have developed a methodology based on block-oriented nonlinear systems that can detect, quantize, and model the battery behavior, accurately. For this purpose, two solid-state coin cells, which have different ionic conductivity at cathode interface are manufactured and excited with multisine input current. The Best Linear Approximation (BLA) method has been used to separate linear frequency response function (FRF) from nonlinear distortion. Then, a Hammerstein-Wiener system have been developed and parametrized to model the nonlinear distortions caused by ionic conductivity variation of the solid electrolyte at the cathode layer. Furthermore, the developed model has been utilized to detect possible fault in the electrode-electrolyte interface based on the nonlinearity level of the measured voltage.

Keywords- block-oriented system identification, All-solid-state Li-Ion battery, ionic conductivity, multisine excitation, Hammerstein-Wiener system

Introduction

The use of lithium-ion batteries in home and industrial applications is rapidly growing. As batteries determine the driving range and power required for acceleration in electric cars, automotive companies are increasing their yearly investment in plug-in hybrid electric vehicles (PHEV) and battery electric vehicles (BEV). Due to the needs of conventional liquid-based electrolyte batteries to sealed packaging for each cell and complicated cooling system for the battery pack, the provided energy density (90–250Wh/kg) is still not high enough which is the main obstacle to increasing the e-drive range [1–4]. In this regard, all-solid-state batteries (SSB) allow the simplification of the packaging and cooling system because of no use of liquid electrolyte and good thermal stability of the solid electrolyte[4,6]. This makes them one of the promising alternates for increasing the energy density of the battery pack up to 500Wh/kg. Regardless of battery type, the efficiency of the battery pack is the main factor in the automotive industry, which must be fulfilled. Many recent publications have focused on the battery management system (BMS), which is the central unit for battery monitoring, state of charge (SoC) and state of health (SoH) estimation [7, 8]. The accurate physical model of the battery cells is the key to reliable and efficient state estimation—a model that can not only estimate the output and/or state of the battery, but also requires minimum processing effort and low price hardware. Researchers have focused on the linear equivalent circuit models (ECM) [9, 10] as they are very fast and easy to implement. In this regard, authors in [10–13] have estimated the SoC and SoH based on the ECM models where the model parameters are identified in the time domain through the hybrid pulse power characterization test (HPPC) [14–16]. Another popular method for parameter identification is based on electrochemical impedance spectroscopy (EIS) in the frequency domain. The Battery cell is scanned with a series of single sines from high to low frequencies [17–19]. However this
method has some drawbacks; first, depending on the lowest frequency, EIS can take several hours and second, in order to minimize the SoC variations for avoiding nonlinear distortions [20], the amplitude of sines must be limited in the range of 5 to 10 mV. Although circuit-based models are somehow linked to the physics of the battery, but they are very general and cannot explain everything [21]. In addition, they are only accurate in the mid-range of SoC, as battery operates linearly.

In many publications, artificial intelligence (AI) has been used for prediction and modeling of lithium ion state of charge and voltage behavior. In [22–24, 35], artificial neural network (ANN) and genetic algorithm (GA) have been used for battery modeling. However, AI based models need many training data and the output accuracy is guaranteed only within the training range. Furthermore, training these algorithms is very time consuming for high dynamic systems and the developed model do not provide any physical interpretation of the system.

In recent years, nonlinear modeling garnered the attention of scientists and engineers as these techniques are flexible and, secondly, most of the systems are nonlinear inherently[25, 26]. The main specific of the nonlinear systems is that output does not change in proportion with the input variations [27]. Many high-tech industries have focused on these models and they have been subject of many scientific papers which have been published in the accredited universities and institutes. In [28–30], electronic amplifiers and photo-diodes have been consider for nonlinear modeling. In another work [31], a nonlinear model of the switched reluctance motor has been developed. Nonlinear modeling is vital for mechanical systems due to their complexity as well as the distortions caused by the hysteresis phenomena [32–34, 54]. In the field of electrochemical systems, specifically batteries, nonlinear models have been considered in the several publications. Authors in [35–39] have claimed that they developed nonlinear models for the batteries, while those are linear parameter varying (LPV) models.

This is very important to determine if a system is linear or not; if it is not, the level of nonlinearity needs to be quantized. Schoukens et al. [40–45] proposed the best linear approximation (BLA) method to detect, qualify, and quantify nonlinearities in a system. They have used periodic zero-mean multisine excitation for system identification. In the case of lithium-ion batteries, Firouz et al. [46] performed BLA analysis on nickel manganese cobalt oxide NMC pouch cell and have extracted linear impedance values from nonlinear distortions in the measured data. However, they only developed a nonparametric model and the extracted linear and nonlinear parts were not parameterized. There are several nonlinear system representations such as the nonlinear differential equations, Volterra series, structured block-oriented, nonlinear state-space, and nonlinear autoregressive exogenous models (NARX) [47–49]. Among those systems, block oriented structures are very strong and popular tools for modeling as they are diverse and flexible and can be linked to the physics of the system [48]. In this type of modeling, the whole system is distributed in linear and nonlinear blocks with a selective configuration such as parallel, series, feedback, or feed forward. Hammerstein and Wiener systems are the subcategory of block-oriented systems, which have rather simple structure and are effective. Researchers in [50, 53] have used Hammerstein and Wiener systems for nonlinear model identification. In the case of battery system identification, only a few papers regarding block-oriented models have been published. In [52] authors use multisine current as the identification excitation and Wiener system is considered for nonlinear modeling. However, the detected nonlinearity is very weak and the identified Wiener function is almost linear. Therefore, the nonlinear distortion for that battery in that condition can be neglected. Authors in [53] have implemented an online parameter estimation for the Wiener battery model. In a similar situation as in [52], the nonlinear behavior of the battery in that paper is weak as well. In [58], authors developed a nonlinear model for battery based on the polynomial nonlinear state-space (PNLSS), which mainly focuses on low SoC (<10%) as nonlinearity is strong on that range.
As can be seen, still there are not enough publications regarding the nonlinear modeling of energy storage systems, specifically block-oriented method, which is a powerful tool of its kind. Nonlinear models let us widen our prospect of the battery’s physical properties and identify its dynamic as well as its limits, which will help us to optimize the design process rather than the try and error in the laboratory. Furthermore, nonlinear models can predict a wider range of cell behavior even in extreme conditions, which can be used for functional safety assessment of battery systems.

1.1. Contribution of the paper

Due to the lack of publications in the field of nonlinear modeling for all solid state lithium ion batteries, this paper has focused on this key issue. As all-solid-state technology is very promising for near future automotive application, and furthermore, still many researches are going on to improve the interface of active material and solid electrolyte. However, in some case of solid electrolyte materials, battery voltage shows strong nonlinearity in high input currents which cannot be predicted with linear electrical models. In order to avoid complicated electrochemical models, this paper utilizes innovative nonlinear models to simulate these behaviors which have less complexity than the physical models. In this research, three nonlinear models—Hammerstein, Wiener, and Hammerstein-Wiener (which is not investigated yet in any other publications)—are developed. Linear and nonlinear parts of the system have been separated and identified based on the BLA method and multisine as the excitation input.

1.2. Organization of the paper

In part 2, the test setup and cells specification, which have been developed for this work, is described. In part 3, the theory of Wiener and Hammerstein systems have been introduced in detail and the identification methodology is explained for each one. In part 4, the introduced methodologies and methods are applied on measured data. Nonlinear methods are developed and validated. And finally, part 5 presents the conclusion and recommended future work.

2. Test setup and input excitation design

2.1. Test setup

As mentioned, due to observed strong nonlinear distortions in SSB voltage when input current is high, these batteries have been selected for further investigations. In this regard, two solid-state coin cells with different material in cathode layer have been prepared as shown in Figure 1. All cells have the same cathode and anode materials—LiNbO3-coated LiCoO2 and graphite. Surface area is 1cm² and the corresponding parts’ thickness and capacity of both cells are similar (0.55 mAh). Both cells have been equipped with LiI-Li2S-P2S5 glass for separator exhibiting ionic conductivity (σ25°C) of 10-3 S/cm. However, the only difference is the ionic conductivity inside of the cathode layer. The ionic conductivity of the cathode layer has been controlled by changing solid electrolyte (SE) materials; in cell number 1, Li2S-P2S5 glass exhibiting ionic conductivity (σ25°C ≈10⁻⁴ S/cm) was equipped, while for cell 2, the solid electrolyte of γ-Li3PS4 (σ25°C ≈10⁻⁵ S/cm) was used.
2.2. Multisine excitation

In this paper, the random phase multisine, which belongs to the extended class of Gaussian signals with a fixed power spectrum, has been used. The idea of adding up several sine waves with a same amplitude and different frequencies would be time saving and provides further information regarding the system. Multisine is a broadband identifier signal which can scan the battery at once and gives the frequency response function (FRF) as output. Based on the application, the frequency content of the multisine can be selected arbitrarily. The voltage response of the battery to input multisine varies depending on the frequency range [46]. This paper’s main interest is to analyze the nonlinear behavior caused by low cathode ionic conductivities; therefore, we focused at low frequencies (f<1Hz) where diffusion reaction has the most contribution on the output voltage.

The general form of the multisine excitation signal is expressed in equation (1) [46].

\[
u(t) = \sum_{n=-N}^{N} A_n/2 e^{i(2\pi f_n t + \theta_n)} = \sum_{n=1}^{N} A_n \cos(2\pi f_n t + \theta_n) \quad (1)
\]

Where \(f_n\) is the \(n^{th}\) excited frequency, \(N\) is the number of excited frequencies, \(t\) is time, \(A_n\) and \(\theta_n\) are the amplitude and phase of each excited frequency, respectively. The amplitude of all sines is identical and their phases are selected randomly between [0,2\(\pi\)]. The number of input samples \(u(t)\) is equal to the length of each experiment sequence \(N_p\) (\(u=[u(k), k=1, ..., N_p]\)). The input \(u(t)\) is repeated \(P\) times, which makes the length of \(u_p(t)\) \(N_p \times P\) times.

The robustness of this method highly depends on the repeating number \(M\) with different phase realization of the multisine excitation and with the same periods and sampling time. Therefore, a set of multisine excitations \(u_p^{[r]}\), \(r=1,...,M\) with \(N_p \times P\) length of each are generated. The results in form of input current have been shown in Figure 2.a and its Fourier transformation in Figure 2.b. The maximum current amplitude is limited to 2.8mA (5C) which is 5 times larger than cell nominal capacity, 0.55mAh. As can be seen in Figure 2.b, each excited sine (blue dots with -70 dB amplitude) are quite larger than the noise level, which appeared as very small amplitude around -160 dB.
As multisine is made from the accumulation of sine waves, it is zero mean, inherently. Therefore, at the end of the measurement, the state of charge remains the same as it was at the beginning of the test. Figure 2.c shows SoC variation for the multisine current in one period. During input excitation design, it has been considered that the SoC variation should not be more than 1%. This constraint helps to neglect OCV variation during multisine test.

3. Linear and Structured Nonlinear Modeling

In real-life, all systems are either weakly or strongly nonlinear in nature. However, depending on the application, they are assumed to be linear or their nonlinearity is neglected. This paper tries to tackle the linear part as well as the nonlinear distortions measured at the output of the battery cells and brings them all together in a unique model. To address those issues, a structured nonlinear system has been considered for coin cells, as shown in Figure 3. The proposed configuration has a transfer function model which handles the linear part of the system. Two nonlinear functions at the input and output of the linear system take care of the nonlinear distortions and, at the end, open circuit voltage (OCV) is added to the estimated voltage. This section will show how we can extract linear response, nonlinear distortion, and noise from the measured current and voltage data.
3.1. Best linear approximation

In the first step, an LTI system (linear time invariant) is extracted from noises and nonlinear distortions. In fact, the periodic characteristic of multisine enables us to approximate linear response through the statistical methods by performing several input current load realizations in several periods. Considering the discretized inputs and outputs measured data in the time domain, we can note [46]:

\[ u^{[r,p]}(k), \ y^{[r,p]}(k) \quad r=1 \ldots M \text{ and } p=1 \ldots P \quad (2) \]

Where \( p \) and \( r \) indicate the \( p \)th period and the \( r \)th realization of the input excitation or of the output response that is considered, respectively. The Fourier spectrum is obtained by applying fast Fourier transformation to both input and output:

\[ U^{[r,p]}, \ Y^{[r,p]} \quad (3) \]

According to the measured current data (Figure 2.a) and comparing the noise level with the target signal, this paper has assumed that the amplitude of the input noise is very small and, therefore, can be neglected, thus inputs in all periods in a realization are identical (\( U^{[r,p]} = U^{[r]} \)). As mentioned, a nonlinear system can be approximated by an LTI dynamic system, known as BLA which is calculated based on the excited frequencies \( n \) as below:

\[ G_{BLA}(j\omega_k) = \arg\min_G \sum_{r=1}^{M} |Y^{[r]}(k) - G(j\omega_k)U^{[r]}(k)|^2 \quad (4) \]

Where \( G(j\omega_k) \) is the FRF, calculated from measured outputs and inputs in the excited frequencies from each realization \( r \):

\[ \hat{G}^{[r]}(j\omega_k) = \frac{Y^{[r]}(k)}{U^{[r]}(k)} \quad (5) \]

Where \( \bar{U}^{[r]} \) and \( \bar{Y}^{[r]} \) are the average of respectively the inputs and the outputs over all periods \( p \) in \( r \)th realization:

\[ \bar{U}^{[r]}(k) = \frac{1}{p} \sum_{p=1}^{p} U^{[r,p]}(k) = U^{[r]}(k) \quad (6) \]

\[ \bar{Y}^{[r]}(k) = \frac{1}{p} \sum_{p=1}^{p} Y^{[r,p]}(k) \quad (7) \]

Considering equations (4) and (5) and by taking the average of the FRF over all M realizations, the BLA is calculated as:

\[ \hat{G}_{BLA}(j\omega_k) = \frac{1}{M} \sum_{r=1}^{M} \hat{G}^{[r]}(j\omega_k) \quad (8) \]
According to the equation (8), in order to calculate \( \hat{G}_{BLA}(j\omega_k) \), at least two realizations are needed. For achieving more robustness and better linear approximation, the number of realizations is very important. Increasing the number of random phase realizations guarantees the reliability of this method as it increases the time needed for measurement and data processing. Not only the number of realizations is important but also the number of periods for each realization also contributes to the quality of results as they provide the possibility to cancel the noise contamination. Furthermore, by applying more periods for each realization, we give a chance to the system to reach the steady-state and eliminate the transient state. The proper number of realizations and periods are determined by dynamic of the system (battery cells) and the application which batteries are going to be used in.

Noise is inevitable in each measurement as these waves are scattered in surrounding spaces. Furthermore, we should not neglect the distortions coming from the nonlinear nature of the system in the measured data. As mentioned, due to the periodic characteristic of multisine, if we suppose there are enough periods per realization, averaging along the periods and realizations will extract noise and nonlinear distortions respectively. The FRF variations are obtained based on the combination of the mean of each single period belongs to realization \( r \), which returns noise variance \( \sigma^2_N(j\omega_k) \) in equation (9).

\[
\sigma^2_N(j\omega_k) = \frac{1}{M \times (p-1)} \sum_{r=1}^{M} \sum_{p=1}^{P} |G^{[r,p]} - G^{[r]}|^2
\]  \hspace{1cm} (9)

The variation of FRF taken over all the different realizations in measured data gives the total variance of BLA \( \sigma^2_{Total}(j\omega_k) \) according to equation (10). Total variance includes the nonlinear response of the battery as well.

\[
\sigma^2_{Total}(j\omega_k) = \frac{1}{M \times (p-1)} \sum_{r=1}^{M} \sum_{p=1}^{P} |G^{[r,p]} - G^{[r]}|^2
\]  \hspace{1cm} (10)

From equation (9), we already calculated the noise variance and total variance (equation 10) includes both noise and nonlinear part of the system. Therefore, the variance of nonlinear distortion is calculated based on equation (11).

\[
\sigma^2_N(j\omega_k) = M[\sigma^2_{Total}(j\omega_k) - \sigma^2_N(j\omega_k)]
\]  \hspace{1cm} (11)

The estimated BLA function in equation (8) was nonparametric and is based on the system response in each excited frequency (many data in FRF). A parametric model of BLA in the form of discrete rational transfer function (\( z \) domain) helps reduce the number of parameters of model and consequently increases the overall computation process.

\[
\hat{G}_{BLA}(j\omega_k, \theta) = \frac{b(j\omega_k)}{a(j\omega_k)} = \frac{b_0 + b_1z^{-1} + b_2z^{-2} + \cdots + b_nz^{-n}}{1 + a_1z^{-1} + a_2z^{-2} + \cdots + a_nz^{-n}}
\]  \hspace{1cm} (12)

The parameters of equation (12) can be identified by using the least square or maximum likelihood estimation methods, which will not be discussed in detail as they are quite well known [14, 57].

### 3.2. Structured nonlinear systems and identification method

As mentioned in the introduction, several modeling approaches represent a nonlinear system. Among those models, this paper focuses on structure-oriented approach. In this method, smaller parts such as linear and nonlinear block(s) are building the whole system. This approach provides a wide range of linear/nonlinear block combinations, which gives us a remarkable degree of freedom to model complicated systems such as chemical devices. Furthermore, in case of li-ion batteries, structured models are quite appropriate for physic-based models as each main or side reactions can be modeled independently [48]. However, using
structures with high complexity makes the parameter identification process very difficult. In this section we investigate three series structures: Hammerstein, Wiener, and Hammerstein-Wiener as shown in Figure 4.

3.2.1. Hammerstein system

The first model structure, which is called the Hammerstein model Figure 4(a), has a series static nonlinearity with the main linear model. The linear model has been identified in the previous section. The Hammerstein function is modeled by a polynomial of order \( p \) (\( f(x) = \alpha_p x^p + \alpha_{p-1} x^{p-1} + \cdots + \alpha_1 x \)) [55]:

\[
h(k) = f_h(u(k), \eta) = \sum_{t=1}^{p} \alpha_t u^t(k)
\]

where \( u(k) \) is the input excitation current, \( h(k) \) is output of static nonlinear function \( f_h \) (in the form of polynomial), and \( \alpha_t \) is the \( t \)th polynomial coefficient of the function of \( p \) order. The output is calculated as:

\[
v_1(k) = \hat{g}_{BLA}(j\omega_k, \theta) h(k) + \varepsilon(k)
\]

\[
= \frac{B(z^{-1})}{A(z^{-1})} h(k) + \varepsilon(k)
\]

Where \( \hat{g}_{BLA}(j\omega_k, \theta) \) is the parametrized BLA function coming from equation (12), \( v_1(k) \) is the output of the linear system and \( \varepsilon(k) \) is the measurement noise. For further simplifications, the denominator of the BLA function is multiplied to the output vector and numerator multiplied to static nonlinearities as below:

\[
A(z^{-1})v_1(k) = B(z^{-1})h(k) + \frac{c(z^{-1})}{d(z^{-1})} e(k)
\]

Where \( \frac{c(z^{-1})}{d(z^{-1})} \) is the noise dynamic. However, we already mentioned that the noise level is very low and could be neglected. Therefore, the input noise term \( e(k) \) will not be considered in the identification process.

3.2.2. Wiener system

In the Wiener system, a static nonlinear function exists right after the linear system block as shown in Figure 4.b. The output voltage of linear block \( (v_1(k)) \) is presented as [55]:

\[
v_1(k) = \hat{g}_{BLA}(j\omega_k, \theta) u(k)
\]
By replacing the identified linear system transfer function in the above equation, we have:

\[ v_l(k) = \frac{B(z^{-1})}{A(z^{-1})} u(k) \]  \hspace{1cm} (17)

If the static nonlinearity in the output of linear model is represented by a polynomial of order \( m \) \( (f(x) = \beta_m x^m + \beta_{m-1} x^{m-1} + \cdots + \beta_1 x) \), then the output of nonlinear block will be:

\[ w(k) = f_w(v_l(k), \eta) = \sum_{t=1}^{m} \beta_t \cdot v_l^t(k) + \varepsilon(k) \]  \hspace{1cm} (18)

Where \( w(k) \) is the output voltage of the Wiener system, \( f_w \) is the static nonlinear function, and \( \beta_t \) is the \( t \)th polynomial coefficient of function \( f_w \) with order of \( m \). If the above equation is rewritten as the function of the input \( u(k) \) by substituting equation (17) into (18):

\[ w(k) = \sum_{t=1}^{m} \beta_t \cdot (\frac{B(z^{-1})}{A(z^{-1})} u(k))^t + \frac{c(q^{-1})}{D(q^{-1})} e(k) \]  \hspace{1cm} (19)

Now the parameters of the above equation are ready to be identified as both output and input coefficients exist in the cost function.

3.2.3. **Hammerstein-Wiener system**

The structure of the Hammerstein-Wiener is composed of a linear system which has been sandwiched between two different static nonlinear functions as shown in Figure 4.c. The overall equation for the Hammerstein-Wiener system is formulated as below [50, 56]:

\[ w(k) = f_w(G_{BLA}(z) f_h(u(k))) \]  \hspace{1cm} (20)

This structure is somehow different from previous configurations as the linear function is covered with two nonlinear functions and no direct access to the linear model is evident initially. In order to break down the whole system to less complex systems, it is split up from the middle in two simpler nonlinear systems as shown in figure 5.

![Fig. 5: Hammerstein-Wiener is divided from middle to simply the identification problem](image)

The unknown parameters that must be estimated are:

\[ a = [a_0, a_1, ..., a_{na}] \]
\[ b = [b_0, b_1, ..., b_{nb}] \]
\[ \zeta = [\zeta_1, \zeta_2, ..., \zeta_P] \]
\[ \gamma = [\gamma_0, \gamma_1, ..., \gamma_m] \]  \hspace{1cm} (21)

Where \( a \), \( b \) are the denominator and numerator coefficients of the linear system transfer function in \( z \) domain \( (A(z^{-1}) \) and \( B(z^{-1}) \)), which has been discussed in equation (12), and \( \zeta \), \( \gamma \) are the parameters of the Hammerstein and Wiener systems \( (f_h \) and \( f_w) \), respectively.. These efforts have been taken to break this complex nonlinear problem into smaller linear sub-systems in order to use simpler identification methods.
The output of the Hammerstein and Wiener functions (Figure 5) are calculated in equations (22) and (23):

\[ h(k) = f_h(u(k), \eta) \quad (22) \]
\[ w(k) = f_w(v_l(k), \eta) \quad (23) \]

Given that the whole system has been split from the middle, the Wiener nonlinear function in the output (equation 23) is inversed as below:

\[ v_l(k) = f_w^{-1}(w(k), \eta) \quad (24) \]

Signal \( s_f(k) \) has been defined at the middle of the system (splitting point), which may be written in the function of output \( w(k) \) and input \( u(k) \). From input to \( s_f(k) \), we have:

\[ s_f(k) = \sum_{i=0}^{nb} b_i \cdot \{ f_h(u[k-i], \zeta_j) \} + \epsilon(k) \quad (25) \]

And from output to \( s_f(k) \):

\[ s_f(k) = a_{0l} \cdot \{ f_w^{-1}(w[k], y_j) \} + \sum_{i=1}^{na} a_l \cdot \{ f_w^{-1}(w[k-l], y_j) \} \quad (26) \]

And finally, by subtracting (25) and (26):

\[ a_{0l} \cdot \{ f_w^{-1}(w[k], y_j) \} = \sum_{i=0}^{nb} b_l \cdot \{ f_h(u[k-i], \zeta_j) \} - \sum_{i=1}^{na} a_l \cdot \{ f_w^{-1}(w[k-l], y_j) \} + \epsilon(k) \quad (27) \]

This assumption helped convert the nonlinear problem to bilinear in the parameters \( a, b, \gamma, \) and \( \zeta \). Then the bilinear problem can be solved by iterative optimization approaches such as least square or particle swarm optimization (PSO).

Though 3.2.1 and 3.2.2 show nonlinearities to be modeled based on the polynomial functions (equations 13 and 18), in this part, the input static nonlinearity (Hammerstein function) is modeled using the Piecewise linear approximation. This method is based on segmented linear regression. Piecewise linear modeling has the highest flexibility for nonlinear function estimation. This method considers the shape and pattern of the distortion rather than the mathematical function estimation such as polynomial functions. In this method, the input data is divided into several arbitrary breaking points \( c \), and then linear regression is performed between each adjacent breaking points and the corresponding output data \( (c_n < u, y \leq c_{n+1}) \). The governing function for each sector is a simple first order linear function as below:

\[ y = K_n + A_n u \quad \text{for} \quad c_n < u \leq c_{n+1} \quad \begin{cases} c_1 = \min(u) \\ c_{n+1} = \max(u) \end{cases} \quad (28) \]

Where \( y \) is the corresponding value for a certain input value of \( u \) in the nth breaking point, \( A_n \) is regression coefficient, and \( K_n \) is the regression constant. It is important that the function continuity at each breaking point must be satisfied. This method gives more degrees of freedom (depending on the number of breaking points) and is proper for models with strong nonlinearities as this method can handle those with less complexity compared with the polynomial functions.

Equation (27) has been rearranged in the form of equation (29) that can be used in the identification algorithm as below:

\[ F(a_l, b_l, \zeta_j, y_j) = bU(k) - aY(k) \quad (29) \]

Furthermore, the nonlinear functions \( f_h \) and \( f_w^{-1} \) have been represented in the form of piecewise linear model as introduced in equation (28). Now, \( U(k) \) and \( Y(k) \) in equation (29) are written as (30) and (31):
maximum current altitude has been limited to 2.

Now the function formulated in equation (29) is ready to be solved by the last square method as:

\[
\begin{align*}
(a_i,b_i,K_{u,i},A_{u,i},K_{y,i},A_{y,i}) &= \text{arg} \min \{F(a_i,b_i,K_{u,i},A_{u,i},K_{y,i},A_{y,i})\}
\end{align*}
\]

So far, the theory behind this type of nonlinear modeling has been explained in detail. Considering the simplicity of the Hammerstein and Wiener systems in compare with pure physical models, they are a strong and flexible solution for nonlinear systems and can be implemented for online parameter identification, Furthermore, they increase the accuracy of state of charge estimation.

4. Results and discussions

In this section, we will apply the introduced nonlinear system modeling to the manufactured solid state coin cells which was described in section 2 and then evaluate the efficiency and accuracy of the Hammerstein-Wiener model in the real-life systems.

As mentioned in part 2, the input multisine excitation has been designed in four realizations and each realization is repeated six times (6 periods). Accumulation of 33 individual sine waves with identical amplitude but randomly selected phase have been implemented in each multisine realization. The frequency of each sine is selected from odd indexes and is in the range of 4mHz up to 1 Hz. The measurement sampling frequency is 10Hz and it is already 10 times larger than the highest multisine frequency, which is 1Hz. The maximum current altitude has been limited to 2.8mA (5C). These current signals are quite zero mean and...
balanced according to Figure 2.a. Figure 6.a shows the input current of coin cells for one of the multisine realizations and Figure 6.b and Figure 6.c indicates the measured voltage corresponding to that input for cell 1 and cell 2 at 50% SoC, respectively.

As it has been indicated in Figure 6.a, the SNR (signal to noise ratio) level of excited frequencies is at least 70dB (≈ 3200 times larger than the noise level), which allows us to neglect the noise in the measured data, which was an assumption in part 3. In Figure 6.b, the SINAD (signal to noise plus distortion ratio) of the measured voltage is approximately 50dB (320 times larger), which it is still large enough to neglect the distortions (accumulation of noise and nonlinear distortions). Contrary, in the case of cell 2, the SINAD of the measured voltage has been considerably reduced to less than 15dB (around 5 times larger than the distortion level), which cannot be neglected anymore as it causes huge errors and uncertainty in the whole model. As the measurement noise is negligible, all anomalies in output voltage is approximated as pure distortion caused by nonlinear nature of the cell 2.

In the next section, linear system as well as the nonlinear distortions will be modeled through the theory, which has been explained in part 3.

4.1. Linear modeling

Impedances of the coin cells have been calculated from measured multisine data using BLA method. Based on equations (8) and (11), approximated linear system and corresponding nonlinear distortion in excited frequencies are shown in Figure 7. Blue and red stars compare the amplitude of impedances of cell 1 and cell 2, respectively. As is expected, the amplitude of linearized impedance of cell 1 increased around 12 times as ionic conductivity reduced approximately 10 times. However, in cell 2, the level of nonlinear distortion has been increased more than 100 times, which is totally unproportioned with the reduced amount of conductivity. In most studies, the nonlinear distortion is being ignored and only linear response is considered for modeling.

![Fig. 7: Bode plot (amplitude) of BLA and nonlinear distortion for cell1 and cell2](image)

The calculated BLA from the measurement in the excited frequencies has been used for the identification of the linear part of the system. According to equation (12), a 3rd order discrete FIR (of finite impulse response) transfer function in $z$ domain has been considered for the linear system. The Bode plot of impedances for both cells is compared with the identified model shown in Figure 8.a. As can be seen, the amplitude of the linear model has a good agreement with the calculated impedances. Furthermore, the error of the impedance’s phase (Figure 8.b) in cell 1 is around 0 and in cell 2, is few degrees. In order to visualize the difference between impedances of two cells (both real and imaginary parts), their Nyquist plots, calculated based on BLA method from same multisine data, have been compared in Figure 8.c. As indicated
in this figure, blue dots and black circles represents cell 1 and 2’s impedance in the form of Nyquist plot, respectively.

The first point is that the curve has been shifted to the right side, which is considered as ohmic resistance increase due to lower ionic conductivity in cell 2.

The second important point is the growth of the diffusion impedance (45º line in Nyquist plot) for real as well as the imaginary part. As we deliberately increased the boundary resistance between solid electrolyte and active material in the cathode, the ohmic resistance increase was expected. However, as ionic conductivity has been decreased, the LiCoO2 particles on the surface of the cathode consume more lithium as concentration is increased [5]. This explains why the imaginary part of impedance for cell 2 has considerably grown due to more lithium diffusion to the particles which are located in proximity of solid electrolyte interfaces and consequently more polarization voltage variation in compare with cell 1.

The identified linear model has been validated with a multisine excitation other than the ones used for the identification algorithm. The input current for both cells is same and the estimated voltages from the linear model are compared to the measured data in Figure 9.a for cell 1 and Figure 9.b for cell 2. The BLA analysis of cell 1 showed nonlinearities to be quite weak; according to Figure 9.a, a linear model is sufficient as the maximum voltage error is around 3mV. Moreover, in cell 2, as was shown in Figure 7, the nonlinearities are very strong and the linear model cannot estimate the output voltage accurately, because of which, in some areas of the voltage curve, the model error reaches to 0.8V (Figure 9.b).

For accuracy and model performance, it is necessary to use nonlinear modeling for system identification such as block oriented modeling as described in part 3. Nevertheless, those systems are the best choices due to their robustness and flexibility in modeling process. These types of modeling provide much more information regarding the essence of the system, its performance, physical behavior, and possible fault prediction, which is vital for safety assessments.
Series Hammerstein-wiener structured models have been chosen to model the nonlinear characteristic of the cell 2 and all three described combinations will be identified and implemented in the following sections. As mentioned, these types of models are very flexible as linear and nonlinear function blocks can be located at different positions and create several possible model configurations. This variety of system configuration allows us to adapt the model based on the application and/or physical structure of the battery. As the linear part has been already identified in section 4.1, it will be use as a base line for all developed model in section 4.2.

4.2. Nonlinear modeling

One of the most basic nonlinear models is the Hammerstein system. In this structure, a nonlinear function comes between the input and linear model. The nonlinear function is identified based on a third order polynomial function as described in equations (13) and (14). Figure 10.a shows measured distortion (blue dots) together with the estimated Hammerstein function (red line). The output of the Hammerstein system in Figure 10.b is compared with measured cell voltage and output of linear model. As can be seen, the Hammerstein model accuracy is 74.5%, which provides 6% less RMS error than the linear model. The shape of the nonlinearity, as indicated in Figure 10.a, shows that the input distortion is not normally distributed, especially in the discharge zone of the curve. Even in that zone, distortions are scattered widely and cannot be estimated with polynomial functions accurately. Obviously, these data is not responding very well to the Hammerstein system as voltage error suggests that we need to go for other configurations.
4.2.2. Wiener model

The Wiener structure is another type of block-oriented system, where the nonlinear function is located after the linear block and before the system output terminals. Based on the procedures explained in section 3.2.2 (equations 18 and 19), a sixth order polynomial function has been identified for the nonlinear function. The output voltage distortion (blue dots) and identified polynomial function (red line) were shown in Figure 11.a. According to Figure 11.b, the accuracy of the predicted voltage through the Wiener model reached 81%, which shows a 6.5% improvement when compared with the Hammerstein model. Clearly, the Wiener system has more compatibility to cell 2 behaviors. Furthermore, the output distortion is less scattered than the distortion observed in the Hammerstein model. According to Figure 11.a, the distortions in the charge zone is almost linear and in the discharge zone, it has a logarithmic pattern. However, the model still is not accurate enough as it couldn’t predict severe voltage drops during discharge.

4.2.3. Hammerstein-Wiener model

The results obtained from two previous sections indicated that the Hammerstein and Wiener systems have their own advantage and disadvantages and are not quite accurate enough for this battery cell. Therefore, we need to go for more advance models, which can provide higher accuracy with a bit more complexity. A Hammerstein-Wiener model is a combination of a Hammerstein function located at the input before linear
block and a Wiener function placed after the linear block at the output. Theoretically, this configuration has the potential to provide a good fit for nonlinear models and estimates the outputs with high accuracy as this system has the third degree of freedom. According to the method explained in section 3.2.3 (equations 29-32), the Hammerstein and Wiener functions were identified and showed in Figure 12. In order to reduce the calculation efforts, piecewise-linear method has been used for nonlinear function estimation. As it was observed before in 4.2.1 and 4.2.2, the positive parts (charging zone) for both functions are totally linear. In contrary, the negative parts (discharge zone) indicate very strong nonlinearities. The Hammerstein curve in Figure 12.a is different from the one seen in Figure 10.a, which will be investigated more in the following sections. However, the patterns of the Wiener curve are almost the same with a slight difference in output range as shown in Figure 12.b.

The Hammerstein-Wiener model has been validated and results are compared with the linear model in Figure 12.c. This model provides much better performance than the two individual models. The total accuracy has reached 86.5% and the model has kept the accumulation of the individual Hammerstein and Wiener accuracies together. Furthermore, the high amplitude voltage drops are almost predicted by the model correctly. One can see that the identified nonlinear functions still have a logarithmic pattern at the discharge zone as it has been observed in case of individual Hammerstein and Wiener systems. It has been proposed and proved that, by using block-oriented nonlinear modeling, the model accuracy and flexibility can be improved remarkably.

![Graphs showing identified functions and comparison with measured voltage](image)

**Fig. 12:** a) identified Hammerstein function, b) identified Wiener function and c) comparison of measured voltage with linear model and Hammerstein-Wiener system output

### 4.3. Physical interpretation of nonlinear functions

After all the efforts for nonlinear modeling, in this part, we will try to use the results of the nonlinear Hammerstein-Wiener system to provide more physical explanations and investigate the possible link to the electrochemical parameter variation from cell 1 to cell 2 due to ionic conductivity reduction.

As mentioned in the test setup, the ionic conductivity of cell 2, deliberately, has been reduced 10 times by using different materials in the interface of cathode active material and solid electrolyte. Therefore, we almost know where the source of nonlinear distortion is and what should be investigated for possible explanations.

According to Figure 13 (a and c), the identified Hammerstein and Wiener functions for cell 1 gives totally linear curves for inputs and outputs (Y=X), respectively, which represents symmetry in cell behavior in
charge and discharge operations. However, in cell 2, the behavior is different. As can be seen in Figure 13 (b and d), the functionality varies from the charge to the discharge phase. In the charging zone of the chart, cell 2 operates quite linearly in both the Hammerstein and Wiener functions. However, when the cell operates at the discharge zone, the nonlinear behavior shows up. In the Hammerstein curve, at Figure 13.b, obviously the input galvanostatic current has been limited by some internal causes and become saturated in the case of values bigger than 2mA. On the other hand, in the Wiener curve in the discharge zone as shown in Figure 13.d, the output voltage drops logarithmic for amplitudes smaller than -0.4 and is reduced way more than it is predicted by the linear model.

The above analysis can be used to evaluate and estimate key electrochemical parameters such as charge-transfer and/or diffusion coefficients. We already explained that the ionic conductivity of the cathode has been reduced and the apparent effect, impedance increment in excited sines, has been seen in Nyquist diagram in Figure 8.c. On the other hand, there is another hidden effect, which is extracted from the Hammerstein-Wiener curves according to Figure 13. During charge, lithium ions migrate from the cathode to the anode and intercalate in graphite particles. Due to high ionic conductivity (10^{-3} S/cm) in the anode and separator layer, no nonlinearity has been detected in the charge zone as shown in Figure 13 (b and d).

**Remark 1:** During discharge, lithium ions intercalate into cathode particles, where the non-uniformities are taking place. As LiCoO2 particles are surrounded by very low ionic conductive materials (10^{-5} S/cm), the LiCoO2 close to the separator are the easiest target as lithium ions cannot reach to the particles located in the depth of the cathode, especially at high current conditions. Therefore, lithium will be consumed by those active particles in interface; if intercalation rate become very high, then the lithium concentration at the surface layer of the active particle reaches maximum amount and causes high voltage drops. These phenomena, so called Nernst diffusion layer, are formulated in equation (33). Therefore, those logarithmic voltage drops (during discharge Figure 13.d) indicated in the Wiener function could originate from the Nernst layer [59].

\[
V_{diff} = \frac{RT}{F} \ln \left( \frac{C_s}{C_{sm}-C_s} \right)
\]  

(33)
Where $C_s$ is the surface concentration, $C_{sm}$ is maximum concentration, R is the universal gas constant, T is the temperature in kelvin, F is the Faraday constant, and $V_{diff}$ is voltage loss due to the Nernst diffusion layer.

Remark 2: The high lithium concentration at the surface limits the charge-transfer current at the boundary of LiCoO$_2$ particles and solid electrolyte as well. The charge-transfer current density $j^{BV}$ is calculated based on the Butler-Volmer equation [60]:

$$j^{BV} = j_0 \cdot \left( e^{\frac{\alpha_o \eta(x)}{u_T}} - e^{-\frac{\alpha_r \eta(x)}{u_T}} \right)$$  \hspace{1cm} (34)

Where $u_T = \frac{RT}{F}$, $j_0$ is the exchange current density at the surface of particle, $\alpha_o$ and $\alpha_r$ are oxidation and reduction charge-transfer coefficient, and $\eta(x)$ is the voltage drop at the interface of solid electrolyte and active particles due to charge-transfer. The exchange current density $j_0$ is high depending on the ionic concentration on the surface of the particle $c_s$ and concentration in the solid electrolyte $c_e$ at the interface as written in below [60]:

$$j_0 = F \cdot k_c \cdot c_e^{\alpha_o} (c_{s,max} - c_s(0,t))^{\alpha_o} (c_s(0,t))^{\alpha_r}$$  \hspace{1cm} (35)

Where $k_c$ is the reaction rate. Equation (35) suggests that when surface concentration increases and reaches maximum $c_{s,max}$, the $j_0$ will be reduced and, consequently, the current density at the interface of electrode materials will be limited. This limitation somehow has been seen in the Hammerstein function in Figure 13.b in the discharge zone. These phenomena can explain why the output of the Hammerstein function has been saturated when the input current increases in certain amounts.

Therefore, it can be interpreted that the Hammerstein function indicates the current saturation because of the charge-transfer limit and the Wiener function explains the severe under voltage drop due to the mass-transfer limit.

5. **Conclusion and future work**

5.1. **Conclusion**

We investigated how the ionic conductivity affects the solid-state battery behavior and how it can be detected from measurable data (voltage and current at the terminal of the cell). In addition, those effects are tackled by nonlinear modeling methods. Based on that assumption, two type all-solid-state coin cells with different ionic conductivity at cathode were prepared. Those cells have been characterized at 60°C with galvanic multisine excitation as input. Measurement results indicated that the measured voltage in cell 2 contains very high levels of nonlinear distortion, despite cell 1, for which the measured data was totally linear. In order to tackle those distortions in the cell electrical model, three structured nonlinear systems—Hammerstein, Wiener, and Hammerstein-Wiener—have been introduced and utilized for cell modeling. It has been shown how each of those systems improved model flexibility and performance. For instance, the Hammerstein-Wiener system increased the accuracy by 18% compared to the conventional transfer function based linear model.

This modeling approach estimates nonlinear functions at input and output of the system, which can be related to the cell’s physical behavior. It was explained due to low ionic conductivity of cell 2 at cathode; the estimated input and output functions in the discharge zone were nonlinear and deviated from the assumed linear line. This paper proposed that the identified Hammerstein and Wiener functions are related to charge and mass-transfer respectively.

5.2. **Future work**
In future publications, more complex nonlinear structures such as parallel and feedback systems will be used for the modeling in order to investigate which model can provide highest accuracy and is the most compatible structure with the physics of the battery. Furthermore, by implementing the nonlinear model for online parameter estimation in battery pack coupled with an online fault detection algorithm, we can increase the safety and reliability of the energy storage system.

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REFERENCES


