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A Review on Electric Vehicle Battery Modelling: from Lithium-ion toward Lithium-Sulfur

Abbas Fotouhi [1,*], Daniel J. Auger [1], Karsten Propp [1], Stefano Longo [1], Mark Wild [2]

1. Centre for Automotive Engineering and Technology, School of Aerospace, Transport and Manufacturing (SATM), Cranfield University, Bedfordshire, MK43 0AL, UK.

2. Oxis Energy Ltd.,Culham Science Centre, Abingdon, Oxfordshire OX14 3DB, UK.

Abstract

Accurate prediction of range of an electric vehicle (EV) is a significant issue and a key market qualifier. EV range forecasting can be made practicable through the application of advanced modelling and estimation techniques. Battery modelling and state-of-charge estimation methods play a vital role in this area. In addition, battery modelling is essential for safe charging/discharging and optimal usage of batteries. Much existing work has been carried out on incumbent Lithium-ion (Li-ion) technologies, but these are reaching their theoretical limits and modern research is also exploring promising next-generation technologies such as Lithium-Sulfur (Li-S). This study reviews and discusses various battery modelling approaches including mathematical models, electrochemical models and electrical equivalent circuit models. After a general survey, the study explores the specific application of battery models in EV battery management systems, where models may have low fidelity to be fast enough to run in real-time applications. Two main categories are considered: reduced-order electrochemical models and equivalent circuit models. The particular challenges associated with Li-S batteries are explored, and it is concluded that the state-of-the-art in battery modelling is not sufficient for this chemistry, and new modelling approaches are needed.

Keywords: Battery Modelling; Electric Vehicle; Lithium Sulfur; Equivalent Circuit; Electrochemical.

1. Introduction

Hybrid vehicles are well-established in the market, and electric vehicles are growing in popularity. This trend is likely to continue for the foreseeable future. There is a strong scientific consensus in the reality of human-made climate change [1],[2], which is reflected in national and international legislation on point-of-use emissions: in Europe, we are already seeing the introduction of stringent regulations. The UK Government has estimated that by 2030, average 'new car' tailpipe emissions will need to fall to around 50-70 g/km – a rough halving from the present day [3]. In discussions with our international academic colleagues, it is clear that in the relatively new, rapidly expanding markets such of China and India, there is a strong consciousness of the need to develop sustainably and without over-dependence on

* Corresponding author. E-mail: a.fotouhi@cranfield.ac.uk; or abfotouhi@gmail.com;

scarce foreign oil imports. There have been many studies that have considered the use of renewable energy sources in next generation of transport systems, and various new technologies have been applied [4]-[6]. The powertrain of the future is likely to be increasingly hybridised, increasingly electrified, and increasingly dependent on high quality, effective and affordable traction batteries.

In the UK, we have some uptake of electric vehicles, but EVs still represent a small market sector and there are challenges associated with their introduction [7]. Although it has been shown that in their present form, electric vehicles are suitable for the day-to-day needs of the typical urban motorist [8], consumers still have concerns about cost, longevity and range [7]. Charging times and safety are also well-known concerns.

Development of energy storage systems is at the heart of vehicle electrification process. Many new technologies for batteries, fuel cells, ultracapacitors, etc. have been developed for implementation in hybrid and electric vehicles. A good example is the Lithium-ion (Li-ion) battery, one of the most widely used technologies in advanced electrified vehicles. Li-ion batteries have been developed to meet different specifications, each with different chemical compositions. Key design objectives for automotive applications include battery energy density, safety and reliability [9]. Among the different types of Li-ion batteries used in EVs are Lithium Cobalt Oxide (LCO), Lithium Manganese Oxide (LMO), Lithium Iron Phosphate (LFP) and Lithium Nickel-Manganese-Cobalt Oxide (NMC) [10]. Table 1 shows some of the battery pack manufacturers and the EVs in which their batteries are used [11].

As Li-ion batteries have been developed to maturity, they have begun to approach their theoretical energy density limits (200-250 Wh/kg [12]). Ongoing electrochemical research on Li-ion batteries aims at increasing cycle life, safety, and other performance characteristics [13]. At the same time, researchers are investigating other types of electrochemical energy storage systems with higher energy density for use in EV applications. One such electrochemical system is the Lithium-Sulfur (Li-S) battery. The Li-S battery offers potential advantages over Li-ion, such as higher energy density, improved safety, a wider operating temperature range, and lower cost (because of the availability of Sulfur); this makes it a promising technology for EV application. However, Li-S technology has not been widely commercialized yet because it suffers from limitations such as self-discharge and capacity fades due to cycling and high discharge current [14]; research into these areas is ongoing.

Battery modelling is a significant task within battery technology development, and is vital in applications. For example, EV range prediction is only possible through the application of advanced battery modelling and estimation techniques to determine current state and predict remaining endurance. In addition, battery modelling is essential for safe charging and discharging, optimal utilization of batteries, fast charging, and other applications. In this study, modelling of batteries is addressed with a focus on their EV applications. Different modelling approaches are reviewed and explained, considering three categories of models: mathematical models, electrochemical models and electrical equivalent circuit networks. The first part of the paper considers these techniques in general, and is potentially useful to a wide range of readers who are interested in understanding the breadth of techniques available for battery modelling, with many different possible applications. The paper then considers our

specific application: hybrid and electric vehicles. This considers modelling approaches which are applicable in EV battery management systems: the discussions presented in this part are mainly focused on low-fidelity models which are fast enough for real-time applications. For this purpose, our review focuses on reduced-order (simplified) electrochemical models, and equivalent circuit network models. The last part of this study specifically considers Li-S battery technology which some researchers view as promising technology for the next generation of hybrid and electric vehicles. Previous studies about Li-S battery modelling are reviewed separately and the challenges of Li-S battery modelling for EV application are discussed.

Table 1: Different Li-ion battery packs manufacturers and EVs in which battery is used [11]

2. Battery Modelling Approaches

There are many studies focused on battery modelling in the literature. Models in can be classified according to the different modelling approaches used. The major categories are mathematical models, electrochemical models and electrical equivalent circuit networks [15],[16]. The literature also contains examples of combined model types such as analytical-electrochemical models [17],[18]. In addition, battery thermal models have been investigated in a number of studies [19]-[21]. Pure thermal models are not in the framework of this study but mixed thermal-electrochemical models are considered as a subset of electrochemical models. Each of the three major categories will be considered in turn.

Before starting the discussions, there is a point which should be noted about the words battery and cell throughout the text. The word 'cell' stands for a single cell which consists of electrodes (anode and cathode), separators, terminals, electrolyte and a case. On the other side, the word 'battery' is used here by its general meaning which can refer to a single cell, a battery module or battery pack.

2.1. Mathematical Models

Models in our first group, 'mathematical models,' can be either *analytical* or *stochastic*. In an analytical model, different physical concepts can be utilized but the common thing in all models is that few equations are used to describe battery properties. As an example of an analytical model, one can refer to the Kinetic Battery Model (KiBaM) [22], which is developed from an understanding of a battery's chemical process kinetics. In this model, the total battery charge is modelled as liquid in two tanks by fraction ratios of c as depicted in Figure 1. The two tanks are the 'available charge' tank, connected directly to the load, and the 'bound charge' tank, which provides charge for the 'available charge' tank. The parameter h_1 represents the battery's state of charge and R_O represents the battery's internal resistance. Supposing the two tanks are connected through a valve with coefficient value of k, the following differential equations describe that how charge changes in each tank.

$$\begin{cases} \dfrac{di}{dt} = -I + k(h_2 - h_1) & where \quad i = h_1.c \\ \dfrac{dj}{dt} = -k(h_2 - h_1) & where \quad j = h_2.(1-c) \end{cases} \tag{1}$$

When a load current (I) is drawn from the battery, the parameter h_1 decreases rapidly and then difference between h_1 and h_2 causes a flow between the tanks until they become equal again. More details of this and other examples of analytical battery models can be found in [15].

Figure 1: Kinetic battery model (KiBaM) [22]

Our second type of mathematical model is the *stochastic* model. Stochastic battery models, such as those developed by Chiasserini and Rao [23],[24], are fast compared to high-fidelity electrochemical models but are still accurate [25]. This type of battery model works on the principle of the discrete-time Markov chain: a Markov process is a memoryless process that one can predict the future of the process based on its present state without knowing its full history. This method can be used to model a random system that its states change based on a transition rule that only depends on the current state of the system.

The literature contains a stochastic version of Kinetic Battery Model, represented as a three-diomensional Markov process [25]. This model has three state parameters (i, j, t). The parameters i and j are defined as depicted in Figure 1 and parameter t is the time since some current was drawn from the battery before the present instant. The battery model moves from one state to the other – this is called a 'transition' – and each transition has an associated probability. Figure 2 illustrates the different state transitions and their probabilities, summarized in the following equations:

$$(i, j, t) \rightarrow \begin{cases} (i+Q, j-Q, t+1) & with\ probability\ of \quad p_r(i, j, t) = q_0.p(t) \\ (i, j, t+1) & with\ probability\ of \quad p_{nr}(i, j, t) = q_0.(1-p(t)) \\ (i-I+J, j-J, 0) & with\ probability\ of \quad q_I \end{cases} \tag{2}$$

A fuller treatment of the stochastic modelling approach and simulation results for the Stochastic Kinetic Battery Model can be found in the original source [25].

Figure 2: State transition diagram of the Stochastic Kinetic Battery Model (KiBaM) [25]

2.2. Electrochemical models

Batteries, as electrochemical systems, can be modelled using physics-based methods. Electrochemical battery models [26],[27] can provide full information on the internal electrochemical dynamics of a battery. Electrochemical battery models consist of a set of coupled partial differential equations (PDEs). These equations explain how the cell's potential is produced and affected by the electrochemical reactions taking place inside the cell. For example, Fick's law of diffusion (equation 6 in Table 2) is used for obtaining solid

concentrations at each electrode and electrolyte concentration. Ohm's law is used to calculate of electrolyte and electrode potentials (equation 3 and 4 in Table 2).

There can be little doubt that good electrochemical battery models are the most accurate among all battery models, as they explain key behaviours of battery at the microscopic scale based on the chemical reactions occurring inside the battery. Considering accuracy as the most important aspect of modelling, these models are excellent and can be used to complement experimental data for evaluation of other models: one advantage of electrochemical models over real data is that internal states are fully observable, allowing 'virtual measurements' of quantities that cannot be measured in practice. The literature contains many examples of electrochemical battery modelling, and not all will be reviewed here: most of them are not directly applicable to our intended application in electric vehicles. Instead, the focus will be in a group of works which consider simplification (order reduction) of these electrochemical battery models. By way of an example, Figure 3 demonstrates a simple schematic of a Li-ion cell containing different parts which are negative and positive electrodes, electrolyte, separator and current collectors [28]. As shown in the figure, the X coordinate is used to determine the cell components' thicknesses. In addition, single particle concentration model is illustrated in a spherical coordinate. The corresponding equations and boundary conditions of this model are stated in Table 2. Model simplification will be discussed later in the paper.

Thermal equations can also be coupled to electrochemical equations. In one source in the literature [29], a thermal-electrochemical model is developed for Li-ion 18650 battery packs. Models of this type are highly detailed, and of very high order. Without any simplification, models of this complexity can only be solved using powerful computational tools and methods such as Computational Fluid Dynamics (CFD) frameworks. One source [30] describes the use of a 313th order CFD model used as a basis for the validation of simpler models. As an alternative to CFD, multiphysics FEM-type modelling environments such as COMSOL Multiphysics can be used, as illustrated in [31]] in which a Li-ion battery with thermal effects is modelled.

Figure 3: Schematic of a Li-ion cell [28]

Table 2: Governing equations of a Li-ion cell electrochemical model [28]

2.3. Electrical equivalent circuit network models

The complexity of the electrochemical models and limitations of the computers in the past, led researchers to investigate another modelling approach called electrical circuit modelling or equivalent circuit (EC) modelling. Nowadays, for many applications, it is important to strike a balance between model complexity and accuracy so that models can be embedded in microprocessors and provide accurate results in real-time [32]. In other words, it is important to have models that are accurate enough, and not unnecessarily complicated. EC modelling is one of the most common battery modelling approaches especially for EV application. Having less complexity, these models have been used in a wide range of applications and various types of batteries [33]-[35].

The EC models are constructed by putting resistors, capacitors and voltage sources in a circuit. The simplest form of an EC battery model is the internal resistance model [36]. The model consists of an ideal voltage source (V_{OC}) and a resistance (R_O) as depicted in Figure 4 in which V_t is battery terminal voltage and I_L is load current.

Figure 4: internal resistance battery model

Adding one *RC* network to the internal resistance model can increase its accuracy by considering the polarization characteristics of a battery. Such models are called 'Thevenin' models [37], illustrated in Figure 5; in this figure, V_t is the battery's terminal voltage, V_{OC} is its Open Circuit Voltage (OCV), I_L is the load current, R_O is the internal resistance, R_P and C_P are equivalent polarization resistance and capacitance respectively. The electrical equation of Thevenin model (1*RC* model) in the Laplace domain is as follows:

$$V_t(s) = V_{OC}(s) - I_L(s)\left(R_O + \frac{R_P}{1 + R_P C_P s}\right) \tag{7}$$

Figure 5: One *RC* network battery model (Thevenin model)

A review of different Thevenin-type battery models is presented in [38]. Adding more *RC* networks to the battery model may improve its accuracy but it increases the complexity too. So a compromise is needed when computational effort and time are vital. This subject is discussed with more details in the following parts.

After selecting the structure of the EC model, parameters of the model need to be determined. A classical method for EC battery model parameterization is Electrochemical Impedance Spectroscopy (EIS) [39],[40]. In this method, an expression for the equivalent impedance of the model from the equivalent circuit is obtained in the frequency domain theoretically, then related to practical data: the electrochemical impedance is the response of an electrochemical system to an applied potential. So an AC voltage is applied to the system and the current is measured in order to calculate the impedance at that frequency. The electrochemical system should be under steady-state conditions during the test. The input's amplitude should be small to avoid nonlinearity effects. However, smaller currents should be avoided as they can be masked by noise. So the system is considered pseudo-linear in a limited range. The frequency of the AC input slowly varies during the test from very small to very large values and the impedance spectrum is plotted as a function of the frequency. As an example, Figure 6 illustrates a system and its impedance-frequency plot. The equivalent impedance of this system is obtained using the following equation:

$$Z_e = R_O + \frac{R_1}{1 + j\omega R_1 C_1} \tag{8}$$

where j is the unit imaginary number, ω is the frequency and other parameters are as depicted in the figure. This formula is easy to relate to the plots obtained in EIS tests, so the

model's parameters can be obtained by a good fitting between theoretical and experimental data. It should be noted that the parameters are obtained under steady-state conditions which means a fixed state of charge (SOC), temperature, etc., so it will be necessary to repeat tests over the range of conditions of interest: there are examples of such tests in the literature [41],[42].

Figure 6: Variation of impedance at different frequencies

One common electric circuit model which is used in EIS tests was proposed by John Edward Brough Randles in 1947 [43]. The model, called Randles circuit model, is illustrated in Figure 7. In cell modelling using the EIS method, each component of the electrical circuit model is related to an electrochemical process in the cell. For example, in Randles model R_b is the bulk resistance of the cell, standing for the electric conductivity of the electrolyte, separator and electrodes. R_{ct} and C_{dl} are the charge transfer resistance and double layer capacitance respectively and they represent the activation polarisation voltage drop. Finally Z_W is the Warburg impedance and stands for the diffusion of the Lithium ions in the cell [44],[45].

Figure 7: Randles circuit

At this stage, a simple visual understanding of the three modelling approaches is useful. Imagine a current impulse is applied to a battery and the battery responds as depicted in Figure 8. Different parts of the battery response should be taken into consideration and be constructed during the modelling process. As seen in the figure, battery voltage response consists of a sudden drop at the beginning and then it goes down through a curve and next, a linear decrease is observed. After the pulse, battery voltage jumps up and then it comes up slowly to reach to open circuit voltage again. Figure 9 demonstrates a schematic of how the different parts of battery response are shaped by different model parameters using each approach.

Figure 8: Current impulse and battery voltage response

Figure 9: Battery response modelling using different approaches

3. Battery Modelling for EV Application

Accurate prediction of range of an EV is a critical issue and a key market qualifier. EV range forecasting relies on the application of suitable modelling techniques. There are a variety of techniques, typically operating at different levels of fidelity and employing different modelling philosophies [46]. The battery model, as a part of the whole vehicle model, plays a significant role in the EV range calculation. Estimation of the EV range without the knowledge of accurate battery SOC is impossible. So in the specific case of battery modelling for EV application, battery SOC estimation is more important than explaining battery I-V characteristics.

In addition to SOC estimation, there are two other vital issues about the application of the battery models in EVs. The first issue is the time. Because of the need for real-time computations in a battery management system (BMS), fast models are preferred rather than complex and accurate models. The second issue is related to the high discharge rates which should be considered in EV battery modelling. Model simplification methods that work well at low discharge rates may not be suitable for EV application. There are two main groups of EV battery modelling studies in the literature. In the first group, electrochemical modelling approach is utilized by applying model simplification techniques and the second group is focused on the EC battery modelling approach.

3.1. Reduced-order electrochemical battery models for EV application

Although, electrochemical battery models are suitable for understanding the electrochemical reactions inside the battery, their complexity often leads to need for more memory and computational effort. So they may not be usable in fast computation and real-time implementation that is needed for EV BMS. This problem has been addressed in many researches by investigating reduced-order models (ROM) that predict the battery behaviour with varying degrees of fidelity [47],[48]. To reduce the order of an electrochemical battery model, discretization techniques can be applied to retain only the most significant dynamics of the full order model [49]. Referring to Table 2, a full order electrochemical battery model consists of a number of nonlinear coupled PDEs. Various discretization techniques are utilized to simplify the full model's PDEs into a set of ODEs of the ROM while keeping the fundamental governing electrochemical equations. In [50], six different discretization methods (listed in Table 3) are addressed and compared for battery system modelling.

Table 3: Battery model discretization methods

Explaining an example of the model order reduction process would be helpful to make the subject clearer. In [56], a single particle model has been investigated for a Li-ion cell that consists of Lithium metal oxide ($LiMO_2$) at positive electrode and Lithiated carbon (Li_xC) at negative electrode. Referring to equation 6 in Table 2, the PDE related to the conservation of Lithium in a single spherical active material particle has been solved analytically. Considering the current and cell's terminal voltage as the input and output of the system respectively, the overall transfer function of the system is obtained as follows. The parameters are defined in Table 4 in which the + and - signs stand for positive and negative electrodes respectively. The model order reduction aims at simplifying this analytical solution with minimum deviation from it.

$$G(s)=\frac{V(s)}{I(s)}=\frac{R_{ct+}}{a_{S+}}\frac{1}{A\delta_{+}}-\frac{R_{ct-}}{a_{S-}}\frac{1}{A\delta_{-}}+\frac{\partial U}{\partial c_{S+}}\frac{1}{A\delta_{+}}\frac{R_S}{a_S FD_{S+}}\left[\frac{\tanh(\beta_{+})}{\tanh(\beta_{+})-\beta_{+}}\right]-\frac{\partial U}{\partial c_{S-}}\frac{1}{A\delta_{-}}\frac{R_S}{a_S FD_{S-}}\left[\frac{\tanh(\beta_{-})}{\tanh(\beta_{-})-\beta_{-}}\right]-\frac{R_f}{A} \tag{9}$$

$$\beta=R_S\sqrt{\frac{s}{D_S}} \tag{10}$$

The above transfer function is infinitely differentiable and can be expanded in a power series at the origin. So in this case, the Padé approximation method is a good choice to discretize the transfer function in order to build a ROM. The order of Padé approximation is a key parameter which affects accuracy of the results. In proportion as the order is higher, the discretized model would be more accurate and complicated both. So the minimum order that get us satisfactory results is desired in each case. In [56], A third order Padé approximation model is developed for each particle transfer function as presented below:

$$Z(s)=K+\frac{b_2s^2+b_1s+b_0}{s^3+a_2s^2+a_1s}+\frac{d_2s^2+d_1s+d_0}{s^3+c_2s^2+c_1s} \tag{11}$$

where the coefficients are stated in Table 5 in which the two parameters C_{+} and C_{-} are defined as follows and K is the total resistance.

$$C_{+}=21\frac{\partial U_{+}}{\partial c_{s,e+}},\ C_{-}=21\frac{\partial U_{-}}{\partial c_{s,e-}} \tag{12}$$

$$K=\frac{R_{ct+}}{a_{S+}}\frac{1}{A\delta_{+}}-\frac{R_{ct-}}{a_{S-}}\frac{1}{A\delta_{-}}-\frac{R_f}{A} \tag{13}$$

So a ROM, that is $Z(s)$, has been obtained for the analytical model presented by $G(s)$ transfer function. Performance of the proposed ROM is analysed in [56] which demonstrates validation of the model with a 10Hz bandwidth. More details of the model order reduction process are available in [62] in which a comprehensive study has been performed to develop reduced-order electrochemical models for a Li-ion battery using discretization methods.

Table 4: Li-ion cell parameters

Table 5: Coefficients of the discretized transfer function

Although the ROMs have many advantages, they may have limitations due to the simplification process which should be considered carefully. For example, application of ROMs in hybrid electric vehicles (HEVs) might differ from the application in the pure EVs

because of the assumptions that used in a ROM. In [49], a seventh-order single particle model has been developed using Padé approximation method. In the model simplification process, linearization around an equilibrium point at 50% SOC is performed. The proposed model performs well but its accuracy is sensitive to the linearization process so that the maximum error increases very much by going far from the equilibrium point. The sensitivity of model to the range of SOC variation might be acceptable for HEVs but not for a pure EV in which SOC varies between zero and 100%. The above mentioned restriction is also found in other studies such as [30] and [56] in which a narrow range of SOC is assumed during the battery model simplification.

In addition to the above mentioned techniques, the battery PDEs (such as presented in Table 2) can be solved using numerical methods. Application of the numerical methods to solve ODEs and PDEs can be found in many text book references. As an example, finite difference method (FDM) for solving PDEs is explained very well in [63]. FDM is not applicable for EV BMS because of the long solution time. But recently, spectral methods have been proposed as an alternative to FDM for solving battery PDEs. Spectral methods have been found to be 10 to 100 times faster than FDM which make them a possible choice for real-time EV BMS application [64].

3.2. Equivalent circuit battery models for EV application

As mentioned before, EC modelling approach is also a good choice for EV applications. In comparison with the electrochemical ROMs which are obtained based on the fundamental equations of the cell, EC models cannot predict cell's internal variables such as the electrolyte potential. In addition, EC models are only available after a battery (or at least a good high-fidelity model) has been made and not during the design process because they need to be developed from test data. On the other hand, EC models have been used in many previous studies for real-time EV BMS application because of their simplicity, speed and acceptable accuracy. In many EV applications, prediction of the cell's internal variables is less important than the ability to get a useful estimate of a cell's SOC. However, it should be noted that a cell's internal variables may provide useful insights for model-based state of health (SOH) estimation of the battery [57]. Thus, the authors believe that both electrochemical ROMs and EC models have potential for EV applications.

3.2.1. EC battery model identification

In addition to EIS method described in section 2.3, system identification techniques are used for battery EC model parameterization. Because these methods are much faster than EIS, they can be utilized in real-time applications such as EV BMS. An identification procedure contains three main parts which are: 1) Model structure selection, 2) Experimental tests design and, 3) Fitness criterion and identification error minimization algorithm selection [65]. EC model structures have already been discussed (section 2.3). Experimental tests may vary however there are common types of test in the literature, notably the charge-discharge current impulse tests. In such a test, a battery is excited by a discharge or charge impulse and is left to rest. Then the battery model parameters are calculated using system identification techniques. For example, Figure 10 illustrates two discharge and charge current pulses

imposed to a single Li-S cell and cell's terminal voltage response. This sample test is performed under a specific condition but it should be noted that battery test procedures should be designed in a way that they cover all possible conditions such as different SOC, temperature, etc.

Figure 10: Discharge and charge current pulses and cell's terminal voltage response

In the third part of the identification process, the model's parameters are determined so that the least difference between the experimental data and the model's output is achieved. Model parameterization can be performed using mathematical algorithms such as Prediction-Error Minimization (PEM) algorithm [65]. In PEM algorithm, the parameters vector (θ) is determined so that the prediction error (ε), defined bellow, is minimized.

$$\varepsilon(t_k,\theta) = y(t_k) - \hat{y}(t_k|t_{k-1};\theta) \tag{14}$$

where $y(t_k)$ is the target output at time k and $\hat{y}(t_k|t_{k-1};\theta)$ is the predicted value of the output at time k using the parameters θ. Then an iterative minimization procedure has to be applied to find the best model parameters values. Because battery parameters are in a limited range and a good initial estimate of them is available, the Gauss-Newton search-scheme works well in this case. Consequently a scalar fitness function is minimized as follows:

$$E_N(\theta) = \det\left(\frac{1}{N}\sum_{k=1}^{N}\varepsilon(t_k,\theta)\,\varepsilon^T(t_k,\theta)\right) \tag{15}$$

3.2.2. EC battery model types

EC battery models can be classified with regard to various aspects such as: 1) Model structure, 2) Model representation, 3) Model adaptation, etc. Starting from the first of these, model structure, different electrical circuit architectures have been tried and tested for EC battery modelling in the literature. Some of these EC battery model structures were introduced in section 2.3. They are usually designed to be accurate as much as possible. This may achieved by adding more parameters to the model. However, an important issue for EV application of the model is simplicity. Indeed, the more parameters are used in the model, the more complex is the model and more computational effort is needed for system identification. So a compromise is essential between accuracy and complexity. As an example, the literature contains a study [66] to find the optimum number of *RC* networks in a battery model with enough precision and suitable complexity. In another study, hysteresis characteristics were also considered in the EC battery model and twelve different EC model structures including combinations of hysteresis effect and different RC networks were addressed and compared [67].

Going to the second criterion, model representation, battery EC models can be formulated so parameters variation over the operating points of interest is described either by look-up tables or by polynomial functions. In the look-up table representation, the battery model data (identified values of model's parameters) is stored in different tables. The look-up tables are

obtained offline from experimental test data. In the alternative representation, polynomial functions are fitted to the test data in order to obtain a number of unknown coefficients. Having the coefficients, the battery model then consists of a set of polynomial functions instead of look-up tables. A number of battery modelling studies in the literature are summarized in Table 6.

Both look-up tables and polynomial functions are fixed because they are obtained offline. So, all operating conditions of interest must be considered during the model parametrization process. These conditions might include various SOC values, temperatures, current rates, etc. However, covering all different conditions needs massive test data and a complete model would contain large number of tables. In addition, consideration of other factors such as battery degradation (due to ageing) makes the problem more complex. A solution for this problem is the ability of adaptation inside the model. Consequently, battery EC models can be also classified with regard to their adaptation capability. An adaptive model can change by obtaining the parameters online using system identification techniques. Examples of such adaptive battery models can be found in [68] and [69].

3.2.3. EC battery model variables

Battery model parameters are not fixed-value constants, and change under different operating conditions. Here the word 'condition' stands for battery SOC, temperature, battery age, etc. So, with respect to the variation of conditions, these variables should be considered in the battery model. In the literature, different variables can be found in battery models. However, there are also fixed battery models that are used when a roughly approximating is needed. In [70] a generic fixed battery model has been developed which is applicable for a variety of battery chemistries including Lead-Acid, Li-ion, Nickel-Cadmium (NiCd) and Nickel-Metal-Hydride (NiMH). Although this model may not be very accurate, its generic feature is an advantage that can be fitted to different battery chemistries.

The most widely used variable in the battery models is battery SOC because it significantly affects battery behaviour. It means that each parameter of the model is considered as a function of SOC as follows:

$$x_i = f_i(SOC), \quad i = 1, 2, ..., N \tag{16}$$

where x_i is the ith parameter of the model, f_i is the function which connects x_i to SOC, and N is the number of parameters. In the literature, the relationship between each parameter and SOC is usually presented using look-up tables or polynomial functions ([68] and [71] in Table 6).

Another important variable that dramatically alters the battery performance is temperature. This effect is so much that can damage the battery so a temperature range is defined by battery manufacturers. Adding temperature as the second variable to f_i function, each parameter of the battery model would be as follows ([72] in Table 6):

$$x_i = f_i(SOC, T), \quad i = 1, 2, ..., N \tag{17}$$

Another factor which can affect the battery behaviour is the current rate. Experiments demonstrate that the whole energy got from the battery during discharging changes by applying different current rates while the other conditions are identical. This is happened because of internal changes that occur inside the battery. For example, higher current rates can increase the battery's internal resistance and consequently lead to more loss of energy. Considering this phenomenon, needs adding one more variable to the model as follows ([44] and [73] in Table 6):

$$x_i = f_i(SOC, T, I), \quad i = 1, 2, ..., N \tag{18}$$

Considering all SOC, temperature and current rate variables would give us a relatively perfect model. Although having such a model might be enough in some cases, there is still another issue which is not considered, battery ageing or cycling degradation. Because of the changes occur inside the battery due to ageing, its performance and consequently its model alters [7]. For example it is demonstrated in [74] that how the cycling can lead to battery internal resistance growth and capacity loss using Thevenin battery model. So, an ageing factor is also essential in a perfect battery model. More generally, battery degradation (due to ageing or whatever) can be considered in a parameter called battery state-of-health (SOH). Adding SOH to the model ([75],[76] and [77] in Table 6), we have:

$$x_i = f_i(SOC, T, I, SOH), \quad i = 1, 2, ..., N \tag{19}$$

A summary of different battery model variables in the literature is presented in Table 6.

Temperature and current are measurable variables so their effects on the model can be easily applied in real-time. The condition is totally different for SOC which is not measurable directly and estimation techniques are required. The accuracy of SOC estimation is vital because battery model's parameters are functions of SOC. There are various techniques in the literature for battery SOC estimation [75],[78]. A conventional method which is also used as a benchmark for evaluation of other techniques, is called Coulomb-Counting (CC) method. In this concept, SOC is calculated by integrating the load current to know how much capacity is used and remained. Although CC method is very useful as a theoretical benchmark, it cannot be utilized in practice because it needs proper initial SOC value. In many applications, batteries do not begin to discharge from fully charged state due to self-discharging or being not originally fully charged [79]. There is also no mechanism to correct for divergence. So, CC method suffers from accumulated errors caused by wrong initial SOC value or noise and measurement errors [80]. Another problem is that the battery capacity can change under various conditions such as temperature variation which leads to an error in CC method. However, CC method can be used as an ideal reference to evaluate other SOC estimation techniques.

Another conventional method for battery SOC estimation is the use of look-up tables or polynomials which relate SOC to the battery's parameters such as the open circuit voltage (OCV). This method also suffers from limitations such as: 1) all possible working conditions should be taken into consideration during the design process and the system would not be able to handle new conditions. So lots of test data is needed to cover all the variables such as

SOC, temperature, etc. 2) this method is not applicable for all battery types such as Li-S battery. The reason is the large flat region in OCV-SOC curve of this type of batteries.

Another group of existing SOC estimation algorithms are recursive adaptive filters such as Kalman filter-based SOC estimators [81]-[83]. In this category, which is the most widely used technique of battery SOC estimation, the estimator works based on the error between the battery output (usually battery terminal voltage) and a battery model's prediction. The prediction error is usually large initially and it decreases gradually after a number of iterations. So, an accurate battery model is needed in this method that is able to predict battery terminal voltage well. The battery model contains the relationship between SOC and other parameters [84],[85]. Comprehensive reviews on the battery SOC estimation methods are available in the literature [86],[87].

Table 6: A summary of different battery model types, variables and parametrization techniques in the literature

4. Lithium-Sulfur Battery: Properties, Modelling and Challenges

The reason that a separate part of this article is allocated to Lithium-Sulfur (Li-S) battery, is the importance of this topic to the automotive industry in the near future. Indeed Li-S batteries with higher energy density, increased safety, wider temperature range of operation and lower cost because of the availability of Sulfur, is a promising technology for EV application. Considering just the first advantage, that is the higher energy density (theoretical capacity of 1675 mAh/g [12]), it would be very much valuable to increase the EV range to three times or more. Figure 11 depicts a good comparison between different battery technologies and the highest specific energy of Li-S cell [88].

Figure 11: Specific energy of Li-S battery in comparison with other types [88]

4.1. Lithium-Sulfur Cell

Li-S cell is a cell with Sulfur at the positive electrode and Lithium metal at the negative electrode. Different reactions may occur inside a Li-S cell, but generally speaking, the discharge process contains gradual reduction of Sulfur to various polysulfides and finally to the low order polysulfides and Lithium Sulfide, and oxidization of Lithium metal to Lithium ions. The opposite direction, that is charging, consists of reduction of the Lithium ions to Lithium, and oxidization of the Sulfide and low order polysulfides to the higher-order polysulfides and Sulfur. A schematic of a Li-S cell and the reactions taking place inside is illustrated in Figure 12 [89]. So the amount of polysulfides or sulphide exist inside the battery at each time depends on SOC. Consequently, the Li-S cell behaves differently from fully charged state to fully discharged state depending on the species inside the cell. This feature produces four distinct regions in the discharge curve of Li-S cell as shown in Figure 13. As seen in the figure, the cell's terminal voltage varies from 2.5 to 1.5 V during discharge and can be modified depending on the choice of cell components.

Figure 12: Schematic of a Li-S cell and the reactions taking place inside [89]

Figure 13: Li-S cell terminal voltage during discharge at C/20 [89]

4.2. Review of Li-S cell modelling

Referring back to the battery model types presented in part 2, almost all Li-S models in the literature are electrochemical and analytical. That is because of the complexity and variety of electrochemical reactions that take place inside this type of battery. In fact, the discharge/charge chemical mechanisms of a Li-S cell are not yet fully understood because of its characteristic features such as the polysulfide shuttle phenomenon [14]. Actually, behaviour of the Sulfur active material in a Li-S cell is very sensitive to the physical and chemical characteristics of the cathode composition and the cell's assembly method both [12],[90]. A sensitivity analysis is performed in [91] for a Li-S mathematical model described in the following.

In [92], a mathematical Li-S cell model is developed which is one of the best references in this area. Eight species are considered in the model which are Li^+, $S_{8(l)}$, S_8^{-2}, S_6^{-2}, S_4^{-2}, S_2^{-2}, S^{-2} and A^-. The model includes electrochemical reactions, dissolution/precipitation reactions, multi-component transport in electrolyte, charge transfer within solid and between solid and liquid and change in cathode and separator porosity due to precipitation. All reactions are listed in Table 7.

Table 7: Reactions in Li-S cell model during discharging [92]

The model can predict the cell's discharge behaviour well with details of species' concentrations. Figure 14 depicts the average concentrations and the average volume fraction of $Li_2S_{(s)}$ in the cathode as functions of discharge capacity in the low and high plateau regions. The above mentioned mathematical model is extended in [93] and [94] by simulating the model under different conditions due to various discharge currents and cycling.

Figure 14: Average concentrations and the average volume fraction of $Li_2S_{(s)}$ in the cathode as functions of discharge capacity [92]

Mechanistic modelling presented in [14] includes the shuttle phenomenon which was not considered in the above mentioned model. 'Shuttle' happens during charging when reduced polysulfides at the negative electrode migrate back to the positive electrode where they are oxidized again. As this phenomenon can affect the cell's cycle life and self-discharge rate, it should be considered in modelling. In [95], a constant is defined called the "shuttle constant" to determine how much of current goes into the shuttle effect. More details of the shuttle mechanism are considered in [14] in which the presented model contains precipitation of Lithium-Sufide on the anode too. Figure 15 illustrates a schematic of the shuttle mechanism and loss of active material in Li-S cell during charging.

Figure 15: Schematic of the shuttle mechanism and loss of active material in a Li-S cell during charging, Black, solid lines: Regular charge; blue, dashed lines: polysulfide shuttle; grey, dotted lines: Lithium Sulfide precipitation at the anode side [14]

As explained in part 2, there is another group of battery models called electrical circuit models. Against Li-ion batteries, there are only a few studies focused on electrical circuit modelling of Li-S batteries. Searching the literature for Li-S cell modelling using electrical circuit approach led us to [96] and [97]. In these studies, the impedance spectroscopy method is utilized to investigate properties of a Li-S cell over the course of cycling. In that study, parameters of a second-order electrical circuit model are determined based on the spectrum results. Each model parameter is obtained as a function of the used capacity. Figure 16 illustrates Li-S cell impedance spectra at different charge levels during discharging [97].

Figure 16: Li-S cell impedance spectra at different charge levels during discharging [97]

4.3. Challenges of Li-S battery modelling for EV application

As mentioned before, for EV application, a fast battery model which is accurate at different SOC levels, subject to various charge/discharge current amplitudes, in a wide range of temperature, etc. is needed. The results in the literature demonstrate that building such a fast and accurate model for a Li-S cell which can deal with different working conditions is difficult. This section is focused on addressing these challenges in Li-S cell modelling for EV application. Against Li-ion batteries, there are not enough studies in the literature in which the reduced-order electrochemical models or equivalent circuit models of Li-S cell are investigated.

One of the most challenging issues in application of Li-S batteries in EVs, is rapid capacity fade due to battery cycling [13],[98]-[100]. The reasons of this phenomenon have been analysed in previous studies. A Li-S cell's capacity may decrease because of composition change on the surface of the Lithium electrode and formation of a layer of solid products on the surface of the sulphur electrode during cycling [96],[101]. Explaining in more details, while the polysulfides S_8^{-2}, S_6^{-2}, and S_4^{-2} are soluble in the electrolyte, the polysulfide ions Li_2S_2 and Li_2S are relatively insoluble. So they may remain within the body of the positive electrode. The shuttling of polysulfide ions (Li_2S_2 and Li_2S) between the electrodes is a major technical issue limiting the self-discharge and cycle life of Li-S battery [89].

As a solution for the above mentioned problem, a new effective method to directly measure shuttle current is presented in [89]. Using this technique, the rate of shuttling process in Li-S cell can be controlled and suppressed and consequently more cycle life is achieved. As another solution, adding Lithium nitrate to the electrolyte has been demonstrated by other researchers to be effective in suppressing the polysulfide shuttle [102]. But the additive Lithium nitrate is consumed over time and after it finishes the shuttle current could change

significantly. In [103], application of an additional carbon-coating onto Sulfur cathodes in Li-S cells is investigated in order to decrease capacity fade. The (binder free) carbon (inter-) layer reduced interfacial resistance (at the cathode/separator interface) increasing capacity and reducing fade due to an increase in Sulfur utilisation, enhancement of electrical contact (with sulfur and polysulfides) and the decrease of active material loss (from the cathode) due to adsorption on the carbon coating. Figure 17 demonstrates battery capacity fade due to cycling with and without carbon-coating. A good summary on different approaches to solve Li-S problems, due to dissolution of polysulfide, is presented in [90] and different electrode and electrolyte materials which have been tested for investigation of Self-discharge characteristics of Li-S cell can be found in [104],[105].

Figure 17: Cycle life properties of Li-S cells tested at 100 mA/g: (a) no-coated, (b) coated for 4 s and (c) coated for 12 s [103]

4. Conclusions

This paper has reviewed techniques for modelling batteries, with a particular focus on three families of techniques: mathematical models, electrochemical models, and equivalent electrical circuit network models. High-fidelity electrochemical models have the potential to offer extreme accuracy and insight, but they are not suitable for most real-time embedded applications. For battery management and range prediction in electric vehicles, there are two families of models that can be used. The first family are simplified 'reduced-order' electrochemical models, which are essentially approximations of their higher-fidelity relatives: obtaining such a model comes at a cost – it requires the creation of an accurate high-fidelity model first – but can provide strong insights into internal variables needed to understand state of health. The second family, the equivalent circuit network models, can be offers less immediate insight into internal state, but can be obtained from experimental data, either through EIS or through the application of system identification techniques. These models can vary in complexity from simple voltage-plus-internal-resistance models, to networks with multiple dynamic elements. Although equivalent circuit network models do not represent internal state directly, they can be parameterized at different operating points, and thereby used to estimate quantities such as state of charge. Many models have parameters which are fixed functions of state and operating point – either implemented as static lookup tables or polynomial functions – but there are families of models that are 'self adapting' and can refine their parameters in response to slowly-changing conditions.

This paper has considered the particular requirements of one 'next generation' battery technology, Lithium-Sulfur. This technology and its particular behaviours were introduced, and the Li-S battery models in the literature were reviewed: these are mostly electrochemical, and there is a lack of literature presenting simple and computationally fast models of Li-S batteries, mainly because the technical challenges associated with Li-S such as 'shuttle' and capacity fade. Further work is required to model and address these issues.

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References

[1] J. Pethica, F. Fox, B. Hoskins, M. Kelly, J. Mitchell, S. Owens, T. Palmer, J. Shepherd, K. Shine and D. Spiegelhalter. *Climate Change: A Summary of the Science*. London: Royal Society, 2010

[2] NASA. "Climate Change: How Do We Know?" http://climate.nasa.gov.uk/evidence, accessed July 30, 2015.

[3] Department of Energy and Climate Change (UK Government). "The Carbon Plan: delivering our low carbon future". London: Department of Energy and Climate Change, 2011.

[4] M.A. Hannana, F.A. Azidina, A. Mohamed, 2014. Hybrid electric vehicles and their challenges: A review. Renewable and Sustainable Energy Reviews 29, 135-150.

[5] A. Fotouhi, R. Yusof, R. Rahmani, S. Mekhilef, N. Shateri, 2014. A review on the applications of driving data and traffic information for vehicles′ energy conservation. Renewable and Sustainable Energy Reviews 37, 822-833.

[6] A. Poullikkas, 2015. Sustainable options for electric vehicle technologies. Renewable and Sustainable Energy Reviews 41, 1277–1287.

[7] D.J. Auger, M.F. Groff, G. Mohan, S. Longo, F. Assadian, 2014. Impact of Battery Ageing on an Electric Vehicle Powertrain Optimisation. Journal of Sustainable Development of Energy, Water and Environment Systems, 2 (4), 350-361.

[8] S. Carroll, C. Walsh, M. Burgess, M. Harris, S. Mansbridge, N. King, L. Bunce, 2013. A report to the technology Strategy Board and the office for Low emission Vehicles by Cenex and Oxford Brookes University, http://www.cenex.co.uk/wp-content/uploads/2014/02/ULCV-summary-report.pdf

[9] M.S. Whittngham, 2004. Lithium batteries and cathode materials. Chemical reviews, 104(10), pp. 4271-4302.

[10] A. Affanni, A. Bellini, G. Franceschini, P. Guglielmi and C. Tassoni, 2005. Battery choice and management for new-generation electric vehicles. IEEE Trans. Ind. Electron., vol. 52, no. 5, pp. 1343-1349.

[11] X. Chen, W. Shen, T. Tu Vo, Z. Cao, A. Kapoor, 2012. An Overview of Lithium-ion Batteries for Electric Vehicles. IEEE Conference on Power & Energy, Ho Chi Minh City.

[12] C Barchasz, F Molton, C Duboc, J C Lepretre, S Patoux, F Alloin, 2012. Lithium/Sulfur Cell Discharge Mechanism: An Original Approach for Intermediate Species Identification. Analytical Chemistry, 84, 3973-3980.

[13] V.S. Kolosnitsyn, E.V. Karaseva, 2008. Lithium–Sulfur Batteries: Problems and Solutions. Russian Journal of Electrochemistry, 44, pp. 506-509.

[14] A. F. Hofmann, D. N. Fronczek, W. G. Bessler, 2014. Mechanistic modeling of polysulfide shuttle and capacity loss in lithium-sulfur batteries. Journal of Power Sources, 259, pp. 300-310.

[15] M.R. Jongerden, B.R. Haverkort. Battery Modeling. Centre for Telematics and Information Technology, University of Twente, TR-CTI, 2008.

[16] A. Shafiei, A. Momeni, S. Williamson, 2011. Battery Modeling Approaches and Management Techniques for Plug-in Hybrid Electric Vehicles. IEEE Vehicle Power and Propulsion Conference, Chicago, IL.

[17] P. Rong and M. Pedram, 2006. An analytical model for predicting the remaining battery capacity of lithium-ion batteries. IEEE Transactions on Very Large Scale Integration Systems, l4(5), pp.441-451.

[18] S. Santhanagopalan, Q. Zhang, K. Kumaresan, and R. E. White. 2008. Parameter Estimation and Life Modeling of Lithium-Ion Cells. J. Electrochem. Soc., 155(4), pp. A345-A353.

[19] C. Mi, B. Li, D. Buck, N. Ota, 2007. Advanced Electro-Thermal Modeling of Lithium-ion Battery System for Hybrid Electric Vehicle Applications. IEEE Vehicle Power and Propulsion Conference, Arlington, TX.

[20] W.B. Gu, C.Y. Wang, 2000. Thermal-Electrochemical Modeling of Battery Systems. J. Electrochem. Soc., 147(8), pp. 2910-2922.

[21] C.Y. Wang, V. Srinivasan, 2002. Computational battery dynamics (CBD) - electrochemical/thermal coupled modeling and multi-scale modeling. Journal of Power Sources, 110, 364-376.

[22] J. Manwell, J. McGowan, 1993. Lead acid battery storage model for hybrid energy systems. Solar Energy, 50, pp. 399-405.

[23] C. Chiasserini, R. Rao. 2001. Improving battery performance by using traffic shaping techniques. IEEE Journal on Selected Areas in Communications, 19(7), pp. 1385-1394.

[24] C. Chiasserini and R. Rao, 2001. Energy efficient battery management. IEEE Journal on Selected Areas in Communications, 19(7), pp. 1235-1245.

[25] V. Rao, G. Singhal, A. Kumar, and N. Navet, 2005. Battery model for embedded systems. International Conference on VLSI Design held jointly with International Conference on Embedded Systems Design, IEEE Computer Society, Washington, DC, USA.

[26] M. Doyle, T.F. Fuller, J. Newman, 1993. Journal of the Electrochemical Society 140, 1526-1533.

[27] T.F. Fuller, M. Doyle, J. Newman, 1994. Journal of the Electrochemical Society 141, 1-10.

[28] K. Smith, C. Y. Wang, 2006. Solid-state diffusion limitations on pulse operation of a lithium ion cell for hybrid electric vehicles. Journal of Power Sources 161, 628-639.

[29] P. Amiribavandpour, W. Shen, A. Kapoor, 2013. Development of thermal-electrochemical model for lithium ion 18650 battery packs in electric vehicles. IEEE.

[30] K. A. Smith , C. D. Rahn, C. Y. Wang, 2007. Control oriented 1D electrochemical model of lithium ion battery. Energy Conversion and Management 48, 2565-2578.

[31] L. Cai, R. E. White, 2011. Mathematical modeling of a lithium ion battery with thermal effects in COMSOL Inc. Multiphysics (MP) software. Journal of Power Sources 196, 5985-5989.

[32] B. Pattipati, C. Sankavaram, K.R. Pattipati, 2011. System Identification and Estimation Framework for Pivotal Automotive Battery Management System Characteristics. IEEE Trans. Syst. Man Cybern. C: Appl. Rev. 41(6), 869-884.

[33] Marc, T.; Oliver, B.; Dirk, U.S. Development of a voltage-behavior model for NiMH batteries using an impedance-based modeling concept. J. Power Sources 2008, 175, 635-643.

[34] A. Fotouhi, K. Propp, D.J. Auger. Electric Vehicle Battery Model Identification and State of Charge Estimation in Real World Driving Cycles. 7th Computer Science and Electronic Engineering Conference, UK, 2015.

[35] H. He, R. Xiong, J. Fan, 2011. Evaluation of Lithium-Ion Battery Equivalent Circuit Models for State of Charge Estimation by an Experimental Approach. Energies, 4, 582-598.

[36] V.H. Johnson, 2002. Battery performance models in ADVISOR. J. Power Sources, 110, 321–329.

[37] Z. M. Salameh, M. A. Casacca, W. A. Lynch, 1992. A mathematical model for lead-acid batteries. IEEE Transactions on Energy Conversion 7(1), 93-98.

[38] S.M. Mousavi G., M. Nikdel, 2014. Various battery models for various simulation studies and applications. Renewable and Sustainable Energy Reviews 32, 477-485.

[39] Haran, B. S., Popov, B. N., and White, R. E., 1998. Determination of the Hydrogen Diffusion Coefficient in Metal Hydrides by Impedance Spectroscopy. J. Power Sources, 75(1), pp. 56-63.

[40] E. Kuhn, C. Forgez, P. Lagonotte, G. Friedrich, 2006. Modelling Ni-mH battery using Cauer and Foster structures. Journal of Power Sources 158, 1490-1497.

[41] J.L. Jespersen, A.E. Tønnesen, K. Nørregaard, L. Overgaard, F. Elefsen, 2009. Capacity Measurements of Li-Ion Batteries using AC Impedance Spectroscopy. World Electric Vehicle Journal, Vol. 3.

[42] C.R. Birkl, D.A. Howey, Model identification and parameter estimation for LiFePO4 batteries. HEVC 2013, University of Oxford, UK.

[43] J. E. B. Randles, 1947. Kinetics of rapid electrode reactions. Discussions of the Faraday Society 1: 11. doi:10.1039/df9470100011. ISSN 0366-9033.

[44] L. Lam, P. Bauer, E. Kelder, 2011. A Practical Circuit-based Model for Li-ion Battery Cells in Electric Vehicle Applications. IEEE 33rd International Telecommunications Energy Conference (INTELEC).

[45] S.S. Zhang , K. Xu, T.R. Jow, 2004. Electrochemical impedance study on the low temperature of Li-ion batteries. Electrochimica Acta 49, 1057-1061.

[46] A. Fotouhi, D.J. Auger, K. Propp, S. Longo, 2014. Simulation for prediction of vehicle efficiency, performance, range and lifetime: A review of current techniques and their applicability to current and future testing standards. 5th IET Hybrid and Electric Vehicles Conference, London, UK.

[47] K.A. Smith, C.D. Rahn, C.Y. Wang, 2008. Model Order Reduction of 1D Diffusion Systems Via Residue Grouping. ASME J Dyn. Syst. Meas. Control, 130(5), p. 011012.

[48] K.A. Smith, C.D. Rahn, C.Y. Wang, 2010. Model-Based Electrochemical Estimation and Constraint Management for Pulse Operation of Lithium Ion Batteries. IEEE Trans. Control Syst. Technol., 18(3), pp. 654–663.

[49] T.R. Tanim, C.D. Rahn, C.Y. Wang, 2015. A Temperature Dependent, Single Particle, Lithium-Ion Cell Model Including Electrolyte Diffusion. Journal of Dynamic Systems, Measurement, and Control, 137, 011005.

[50] Shi, Y., Prasad, G. K., Shen, Z., and Rahn, C. D., 2011. Discretization Methods for Battery Systems Modeling. American Control Conference, CA.

[51] B. Gebhart, Heat Conduction and Mass Diffusion. New York, NY: McGraw-Hill, 1993.

[52] V. R. Subramanian, J. A. Ritter, and R. E. White, “Approximate solutions for galvanostatic discharge of spherical particles,” Journal of the Electrochemical Society, vol. 148, no. 11, pp. E444–E449, 2001.

[53] V. R. Subramanian, D. Tapriyal, and R. E. White, 2004. A boundary condition for porous electrodes. Electrochemical and Solid-State Letters, 7(9), pp. A259–A263.

[54] S. Santhanagopalan, Q. Guo, P. Ramadass, and R. E. White, 2006. Review of models for predicting the cycling performance of lithium ion batteries. Journal of Power Sources, 156(2), pp. 620-628.

[55] J.C. Forman, S. Bashash, J.L. Stein, H.K. Fathy, 2011. Reduction of an Electrochemistry-Based Li-Ion Battery Model via Quasi-Linearization and Padé Approximation. Journal of the Electrochemical Society 158, A93-A101.

[56] G.K. Prasad, C.D. Rahn, 2012. Development of a First Principles Equivalent Circuit Model for a Lithium Ion Battery. ASME Paper No. DSCC2012-MOVIC2012-8607.

[57] J. Marcickia, M. Canovaa , A.T. Conliska , G. Rizzoni, 2013. Design and parametrization analysis of a reduced-order electrochemical model of graphite/LiFePO4 cells for SOC/SOH estimation, Journal of Power Sources 237, 310-324.

[58] J. N. Reddy and D. K. Gartling, The finite element method in heat transfer and fluid dynamics. Boca Raton, FL: CRC Press, Ltd., 2000.

[59] G. G. Botte, V. R. Subramanian, R. E. White, 2000. Mathematical modeling of secondary lithium batteries. Electrochimica. Acta, 45, 2595-2609.

[60] Y. Yener and S. Kakac, Heat Conduction. New York, NY: Taylor and Francis, 2008.

[61] V.R. Subramanian, V.D. Diwakar, D. Tapriyal, 2005. Efficient Macro-Micro Scale Coupled Modeling of Batteries. Journal of the Electrochemical Society 152, A2002-A2008.

[62] K. A. Smith, 2006. ELECTROCHEMICAL MODELING, ESTIMATION AND CONTROL OF LITHIUM ION BATTERIES. PhD Thesis, Pennsylvania State University.

[63] R. J. LeVeque, Finite difference methods for ordinary and partial differential equations : steady-state and time-dependent problems. Philadelphia, PA: Society for Industrial and Applied Mathematics, c2007.

[64] A. Bizeray, S.R. Duncan , D.A. Howey, 2013. Advanced battery management systems using fast electrochemical modelling, IET Hybrid and Electric Vehicles Conference (HEVC).

[65] L. Ljung, System Identification - Theory for the User, Prentice Hall, New York,1987.

[66] H. He, R. Xiong, H. Guo, S. Li, 2012. Comparison study on the battery models used for the energy management of batteries in electric vehicles. Energy Conversion and Management, 64, 113-121.

[67] X. Hu, S. Li, H. Peng, 2012. A comparative study of equivalent circuit models for Li-ion batteries. Journal of Power Sources 198, 359-367.

[68] H. Rahimi-Eichi, M.Y. Chow, 2012. Adaptive Parameter Identification and State-of-Charge Estimation of Lithium-Ion Batteries. IEEE , 4012-4017.

[69] G. LIU, M. OUYANG, L. LU, L. XU, J. LI, 2012. Online Monitoring of Lithium-ion Battery Aging Effects by Internal Resistance Estimation in Electric Vehicles. Chinese Control Conference, Hefei, China.

[70] O. Tremblay, L.A. Dessaint, A.I. Dekkiche, 2007. A Generic Battery Model for the Dynamic Simulation of Hybrid Electric Vehicles. IEEE Vehicle Power and Propulsion Conference, Arlington, TX.

[71] M. Chen, G. A. Rincon-Mora, 2006. Accurate Electrical Battery Model Capable of Predicting Runtime and I–V Performance. IEEE TRANSACTIONS ON ENERGY CONVERSION, 21(2), 504-511.

[72] C. Antaloae, J. Marco, F. Assadian, 2012. A Novel Method for the Parameterization of a Li-Ion Cell Model for EV/HEV Control Applications. IEEE TRANSACTIONS ON VEHICULAR TECHNOLOGY, 61(9), 3881-3892.

[73] R.C. Kroeze, P.T. Krein, 2008. Electrical Battery Model for Use in Dynamic Electric Vehicle Simulations. IEEE Power Electronics Specialists Conference, Rhodes.

[74] J. Nadeau, M.R. Dubois, A. Desrochers, N. Denis, 2013. Ageing estimation of lithium-ion batteries applied to a three-wheel PHEV roadster. IEEE Vehicle Power and Propulsion Conference, Beijing.

[75] A Papazoglou, S Longo, D Auger, F Assadian, 2014. Nonlinear Filtering Techniques Comparison for Battery State Estimation, Journal of Sustainable Development of Energy, Water and Environment Systems, 2(3), 259-269.

[76] L. Serrao, Z. Chehab, Y. Guezennec, G. Rizzoni, 2005. An Aging Model of Ni-MH Batteries for Hybrid Electric Vehicles. IEEE Conference on Vehicle Power and Propulsion.

[77] A. Millner, 2010. Modeling Lithium Ion Battery Degradation in Electric Vehicles. IEEE Conference on Innovative Technologies for an Efficient and Reliable Electricity Supply, Waltham, MA.

[78] J. Xu, B. Cao, J. Cao, Z. Zou, C. C. Mi, Z. Chen, 2013. A Comparison Study of the Model Based SOC Estimation Methods For Lithium-Ion Batteries. IEEE Vehicle Power and Propulsion Conference, Beijing, China.

[79] C.H. Cai, D. Du, Z.Y. Liu, Battery State-of-Charge (SOC) Estimation Using Adaptive Neuro-Fuzzy Inference System (ANFIS), IEEE 2003.

[80] K. Kutluay, Y. Cadirci, Y. S. Ozkazanc, and I. Cadirci, "A new online state-of-charge estimation and monitoring system for sealed lead-acid batteries in Telecommunication power supplies," Industrial Electronics, IEEE Transactions on, vol. 52, pp. 1315-1327, 2005.

[81] G.L. Plett, 2004. Extended Kalman filtering for battery management systems of LiPB-based HEV battery packs: Part 1. Background. Journal of Power Sources, vol. 134, pp. 252-261.

[82] G.L. Plett, 2006. Sigma-point Kalman filtering for battery management systems of LiPB-based HEV battery packs, Part 2: Simultaneous state and parameter estimation. Journal of Power Sources 161, pp. 1369-1384.

[83] H. Rahimi-Eichi, F. Baronti, M.Y. Chow, 2014. Online Adaptive Parameter Identification and State-of-Charge Coestimation for Lithium-Polymer Battery Cells. IEEE TRANSACTIONS ON INDUSTRIAL ELECTRONICS 61(4), pp. 2053-2061.

[84] H. He, R. Xiong, X. Zhang, F. Sun, J.X. Fan, 2011. State-of-Charge Estimation of the Lithium-Ion Battery Using an Adaptive Extended Kalman Filter Based on an Improved Thevenin Model. IEEE Transactions on Vehicular Technology, 60 (4), pp. 1461-1469.

[85] J. Xu, C. C. Mi, B. Cao, J. Deng, Z. Chen, S. Li, 2015. The State of Charge Estimation of Lithium-Ion Batteries Based on a Proportional Integral Observer. IEEE Transactions on Vehicular Technology.

[86] S. Piller, M. Perrin, A. Jossen, Methods for State-of-charge Determination and Their Applications. Journal of Power Sources 2001, 96, pp.113-120.

[87] M. Ugras Cuma, T. Koroglu, 2015. A comprehensive review on estimation strategies used in hybrid and battery electric vehicles. Renewable and Sustainable Energy Reviews 42, 517-531.

[88] OXIS Energy company web site, accessed July 7, 2015, http://www.oxisenergy.com/

[89] D. Moy, A. Manivannan, S. R. Narayanan, 2015. Direct Measurement of Polysulfide Shuttle Current: A Window into Understanding the Performance of Lithium-Sulfur Cells. The Electrochemical Society, 162 (1) A1-A7.

[90] S. S. Zhang, 2013. Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and solutions. J. Power Sources 231, 153-162.

[91] M. Ghaznavi, P. Chen, 2014. Sensitivity analysis of a mathematical model of lithium-sulfur cells, part I: Applied discharge current and cathode conductivity. Journal of Power Sources 257, 394-401.

[92] K. Kumaresan, Y. Mikhaylik, R. E. White. A Mathematical Model for a Lithium-Sulfur Cell. Electrochemical Society, 155 (8) A576-A582, 2008.

[93] J.P. Neidhardt, D.N. Fronczek, T. Jahnke, T. Danner, B. Horstmann, W.G. Bessler, 2012. A Flexible Framework for Modeling Multiple Solid, Liquid and Gaseous Phases in Batteries and Fuel Cells. J. Electrochem. Soc. 159 (9), A1528-A1542.

[94] D.N. Fronczek, W.G. Bessler, 2013. Insight into lithium-sulfur batteries: Elementary kinetic modelling and impedance simulation. J. Power Sources 244, 183-188.

[95] Y. Mikhaylik, J. Akridge, J. Electrochem. Soc. 151 (11) (2004) 1969-1976.

[96] V.S. Kolosnitsyn, E.V. Kuzmina, E.V. Karaseva , S.E. Mochalov, 2011. A study of the electrochemical processes in lithium–sulphur cells by impedance spectroscopy. Journal of Power Sources 196, 1478-1482.

[97] V. S. Kolosnitsyn, E. V. Kuzmina, E. V. Karaseva, and S. E. Mochalov, 2011. Impedance Spectroscopy Studies of Changes in the Properties of Lithium–Sulfur Cells in the Course of Cycling. Russian Journal of Electrochemistry, 47(7), 793-798.

[98] R.D. Rauh, K.M. Abraham, G.F. Pearson, J.K. Surprenant, S.B. Brummer, 1979. A Lithium/Dissolved Sulfur Battery with an Organic Electrolyte. Journal of the Electrochemical Society 126, pp. 523-527.

[99] H. Yamin, E. Peled, 1983. Electrochemistry of a nonaqueous lithium/sulfur cell. Journal of Power Sources 9, 281-287.

[100] H. Yamin, A. Gorenshtein, J. Penciner, Y. Sternberg, E. Peled, 1988. Lithium Sulfur Battery: Oxidation/Reduction Mechanisms of Polysulfides in THF Solutions. Journal of Electrochemical Society 135, pp. 1045-1048.

[101] V.S. Kolosnitsyn, E.V. Karaseva, A.L. Ivanov, 2008. Electrochemistry of a lithium electrode in lithium polysulfide solutions. Russian Journal of Electrochemistry 44(5), pp. 564-569.

[102] Y. V. Mikhaylik, 2009. U.S. Patent, patent No. 7,553,590.

[103] Y.J. Choi, Y.D. Chung, C.Y. Baek, K.W. Kim, H.J. Ahn, J.H. Ahn, 2008. Effects of carbon coating on the electrochemical properties of sulfur cathode for lithium/sulfur cell. Journal of Power Sources 184, pp. 548-552.

[104] H.S. Ryu, H.J. Ahn, K.W. Kim, J.H. Ahn, J.Y. Lee, E.J. Cairns, 2005. Self-discharge of lithium-sulfur cells using stainless-steel current-collectors. Power Sources, 140, 365-369

[105] H.S. Ryu, H.J. Ahn, K.W. Kim, J.H. Ahn, K.K. Cho, T.H. Nam, 2006. Self-discharge characteristics of lithium/sulfur batteries using TEGDME liquid electrolyte. Electrochimica Acta 52(4), 1563-1566.

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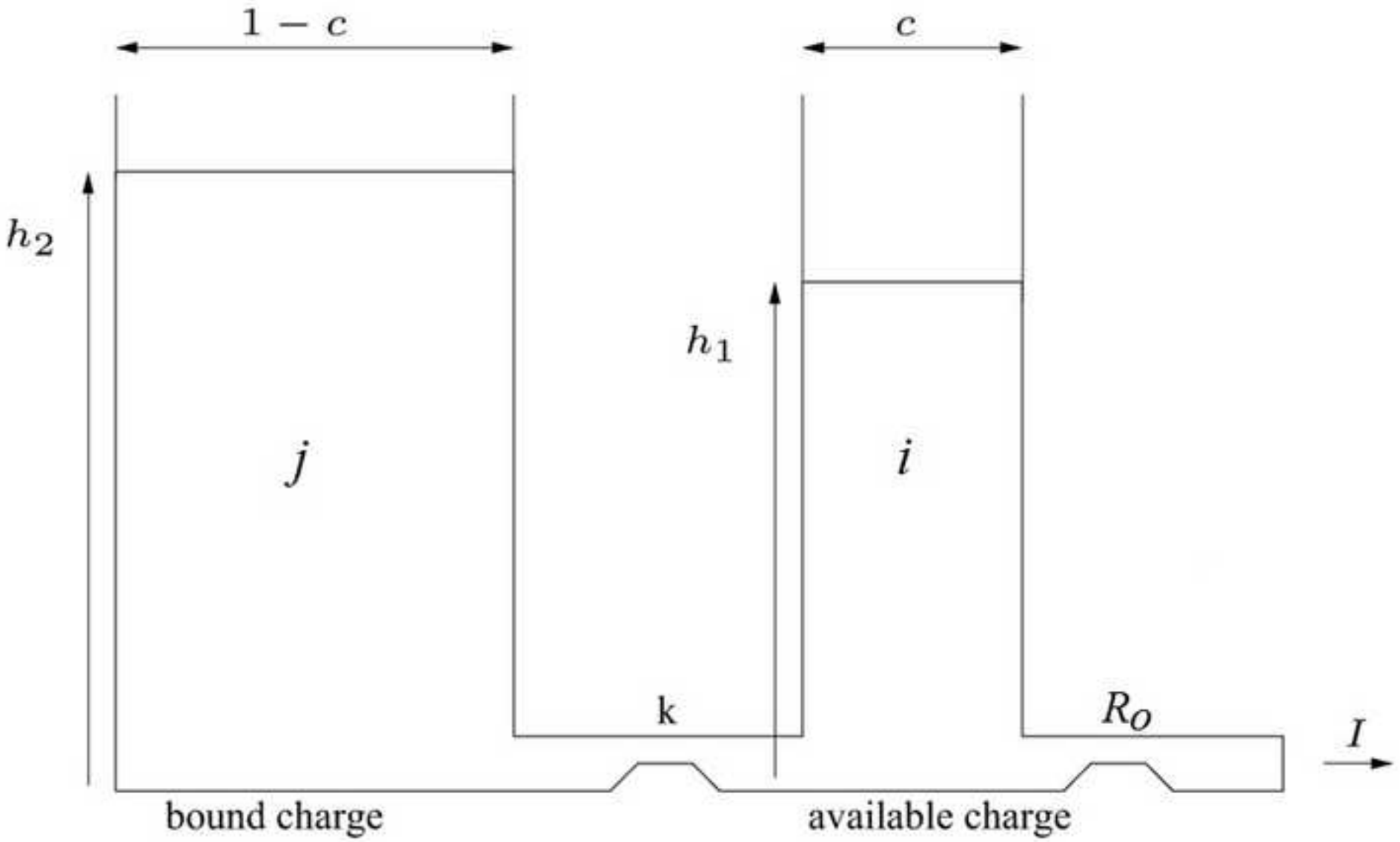

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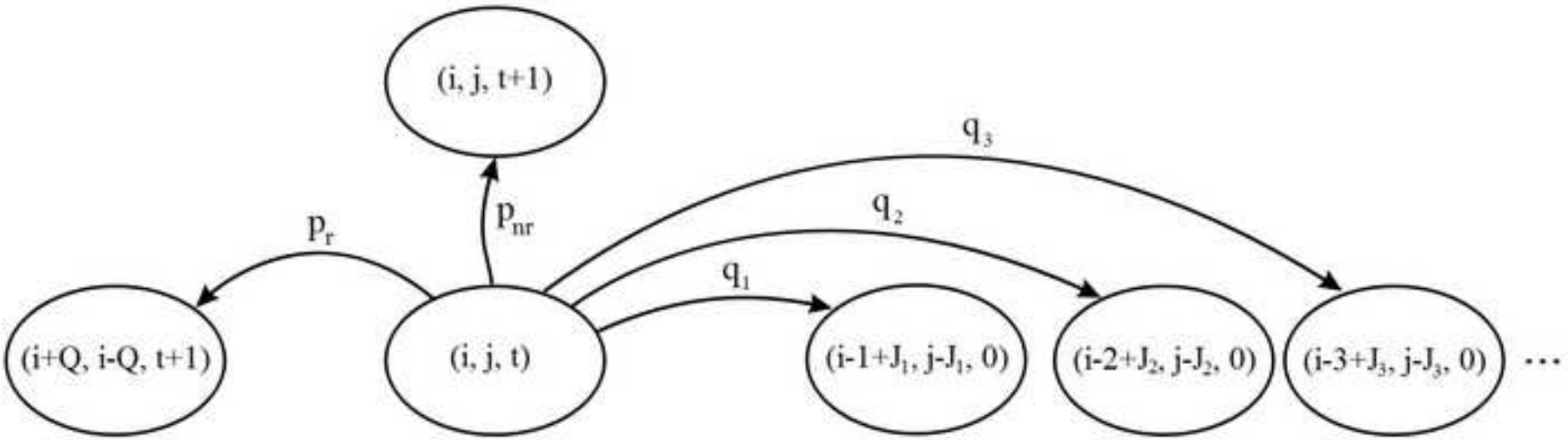

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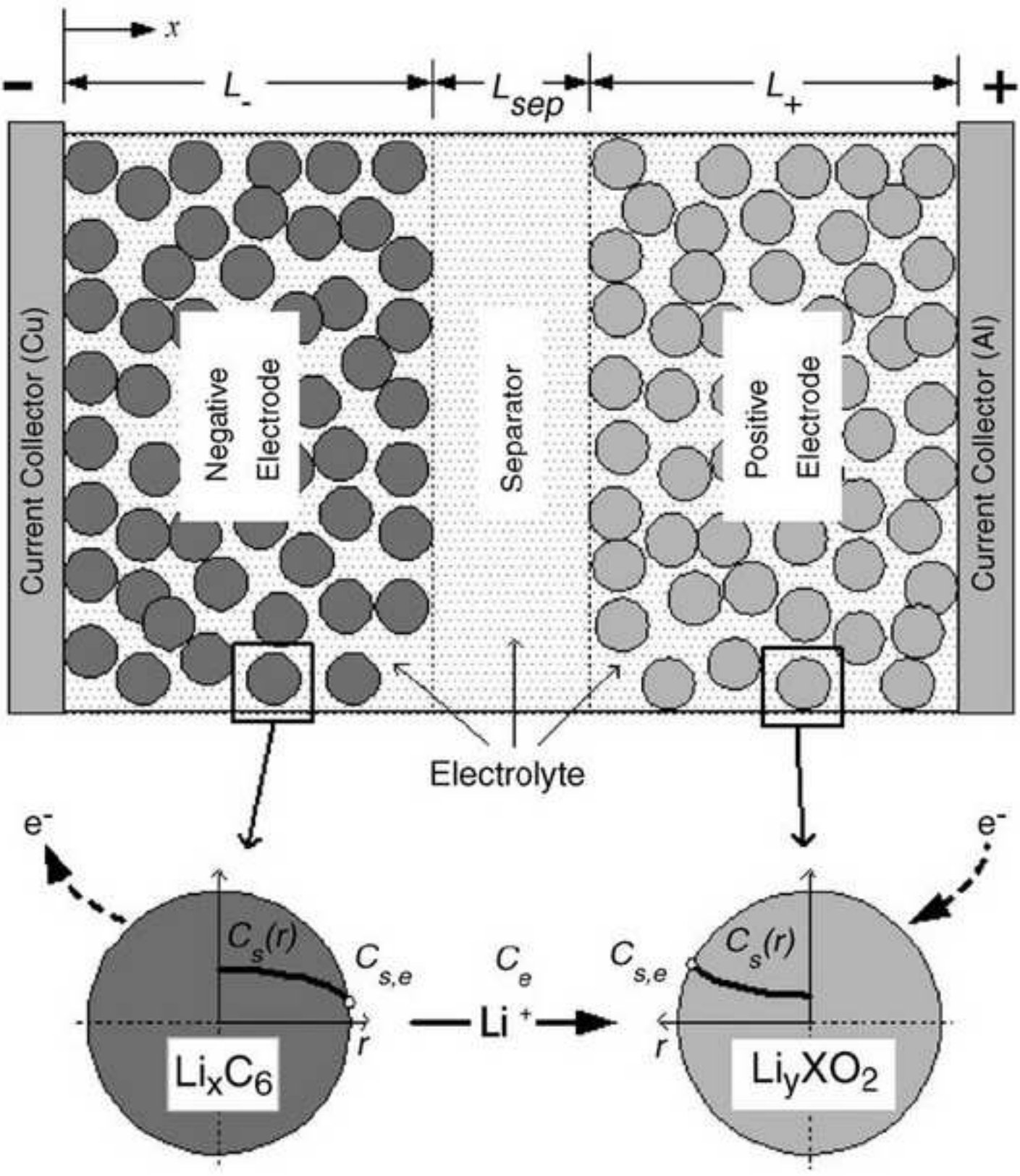

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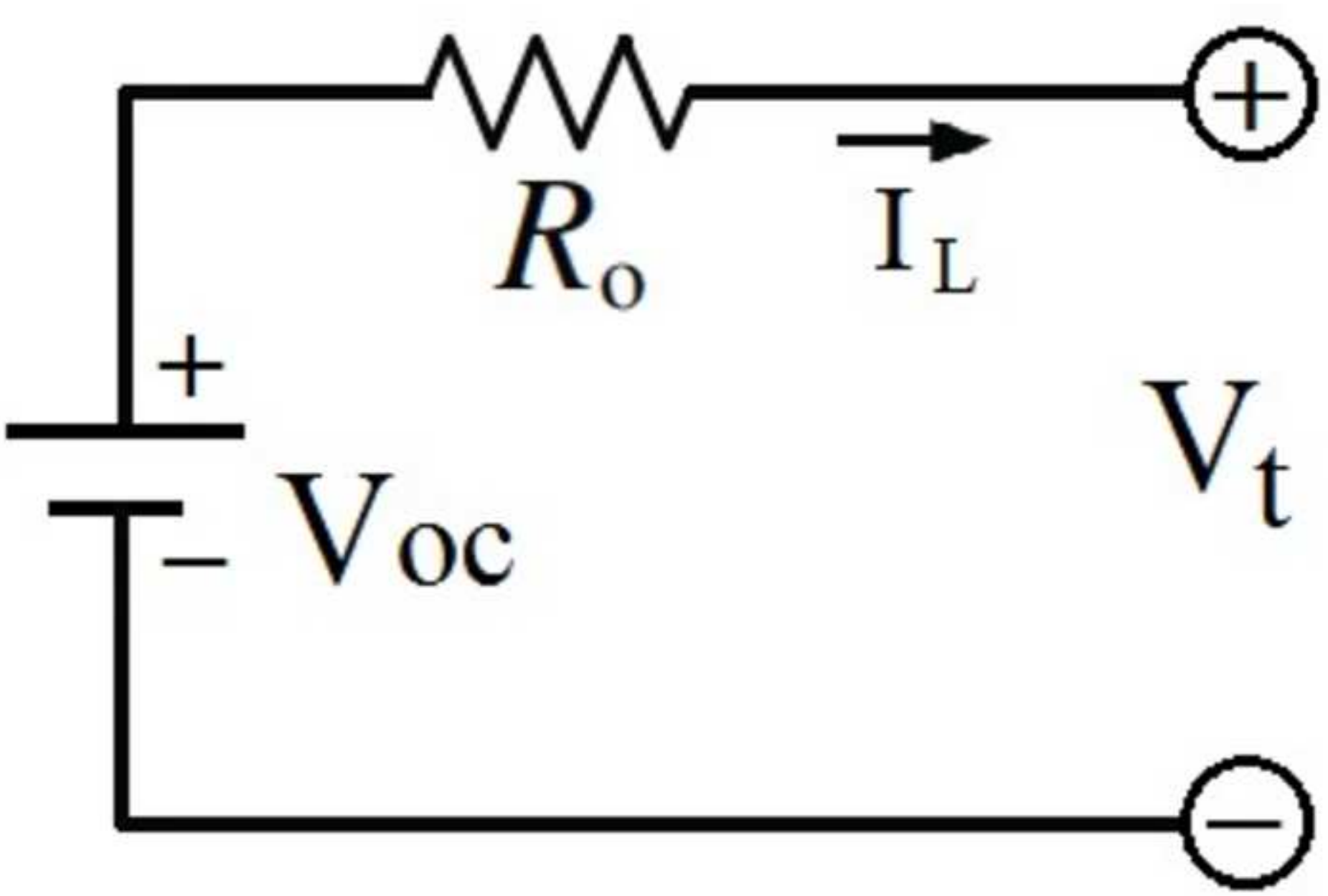

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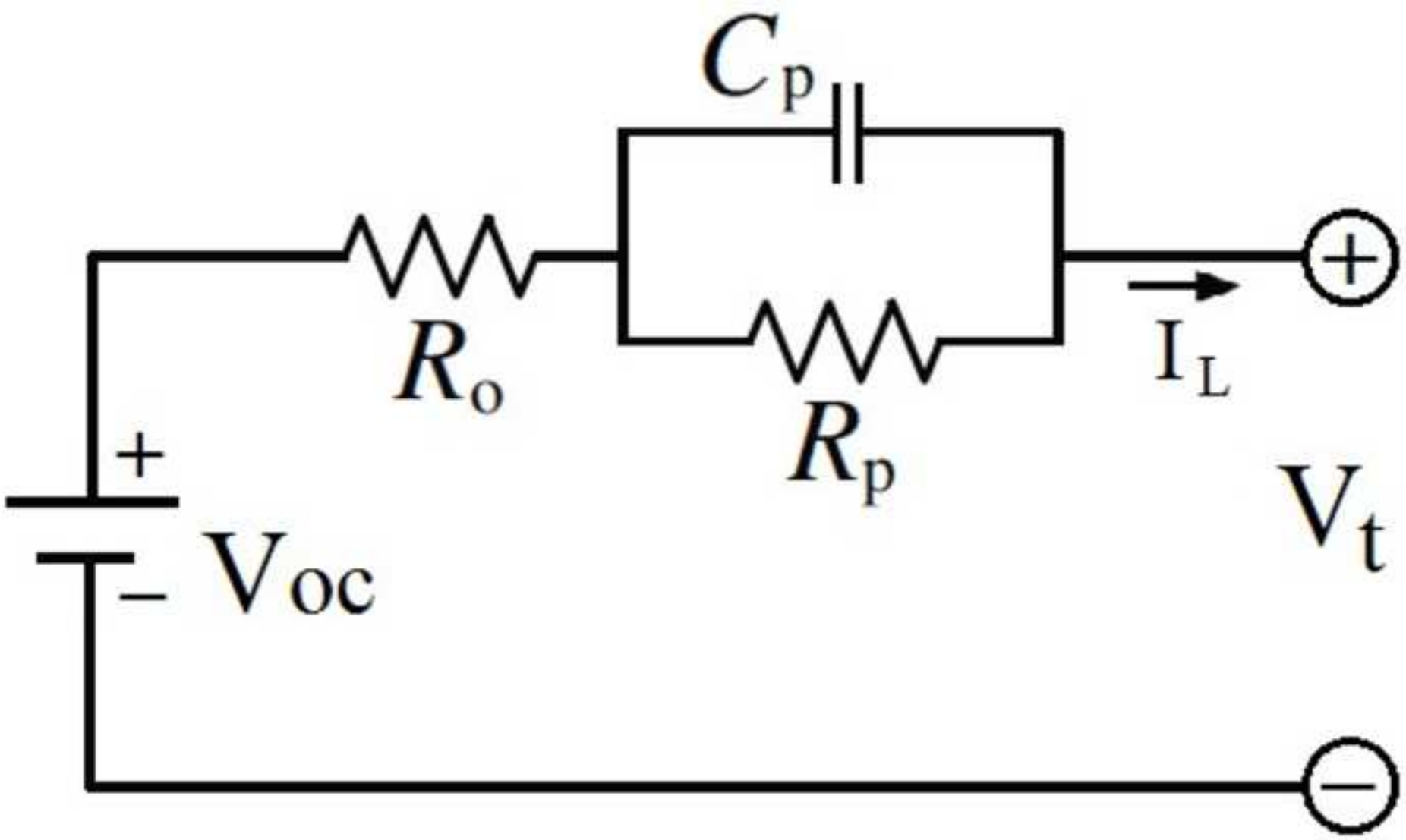

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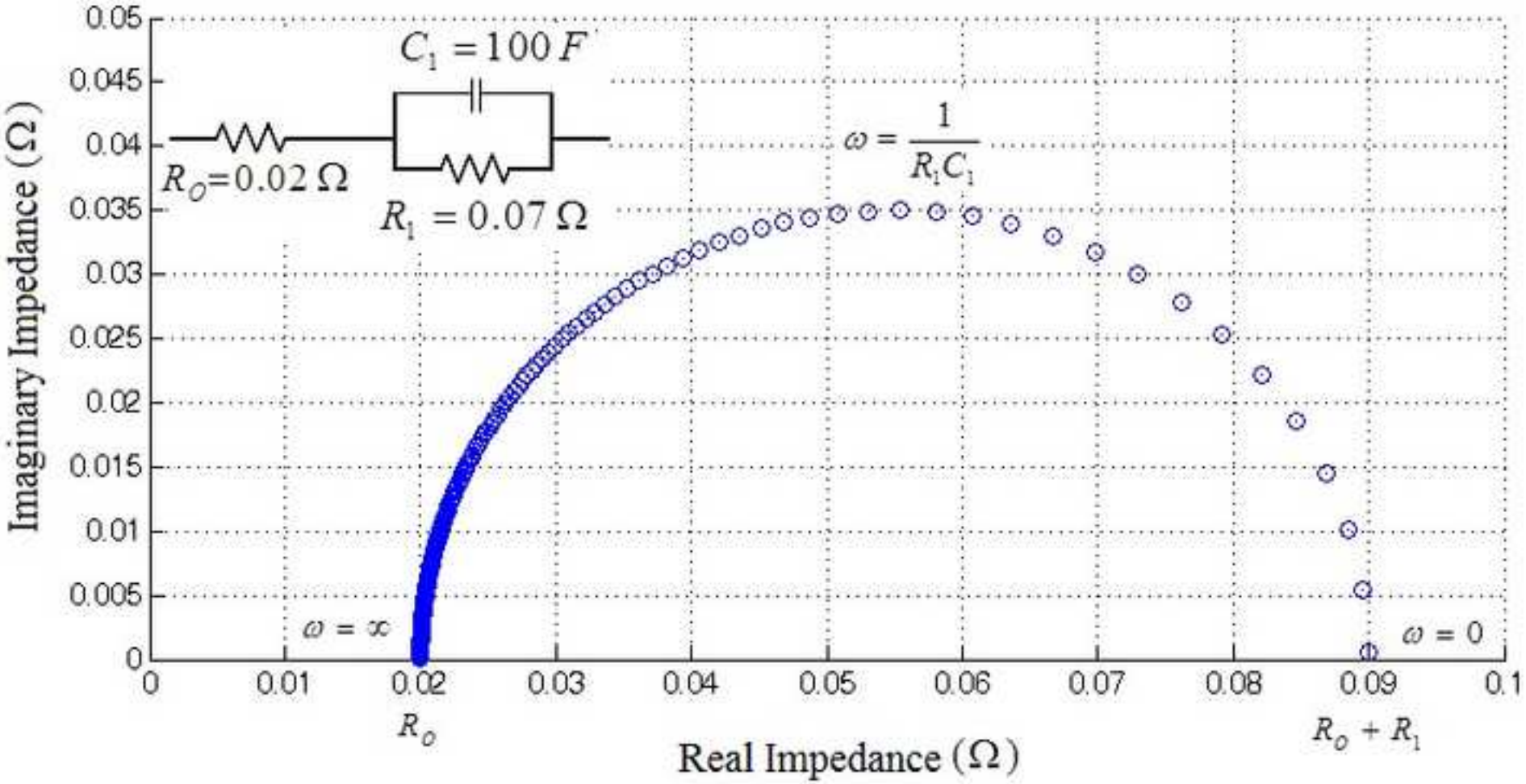

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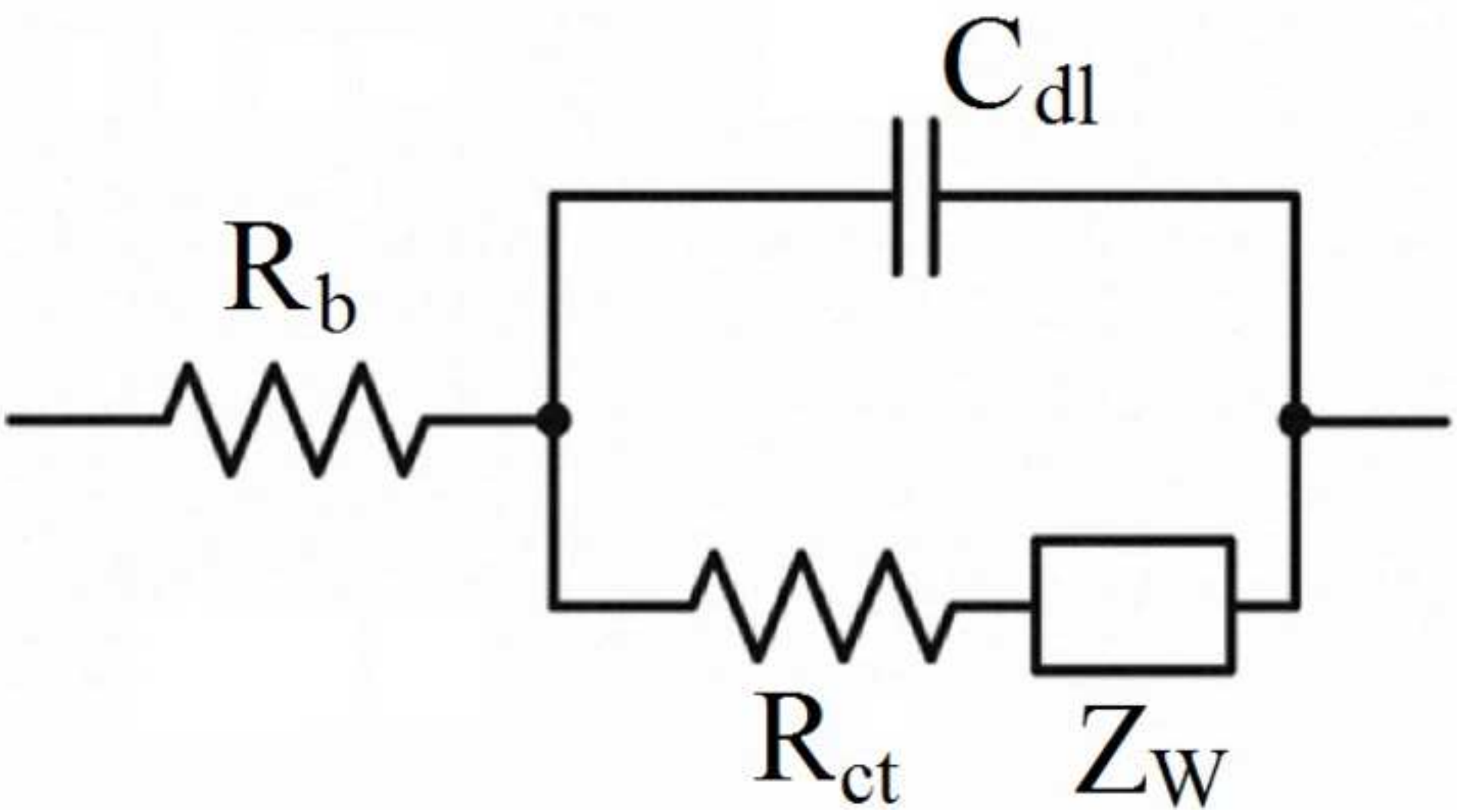

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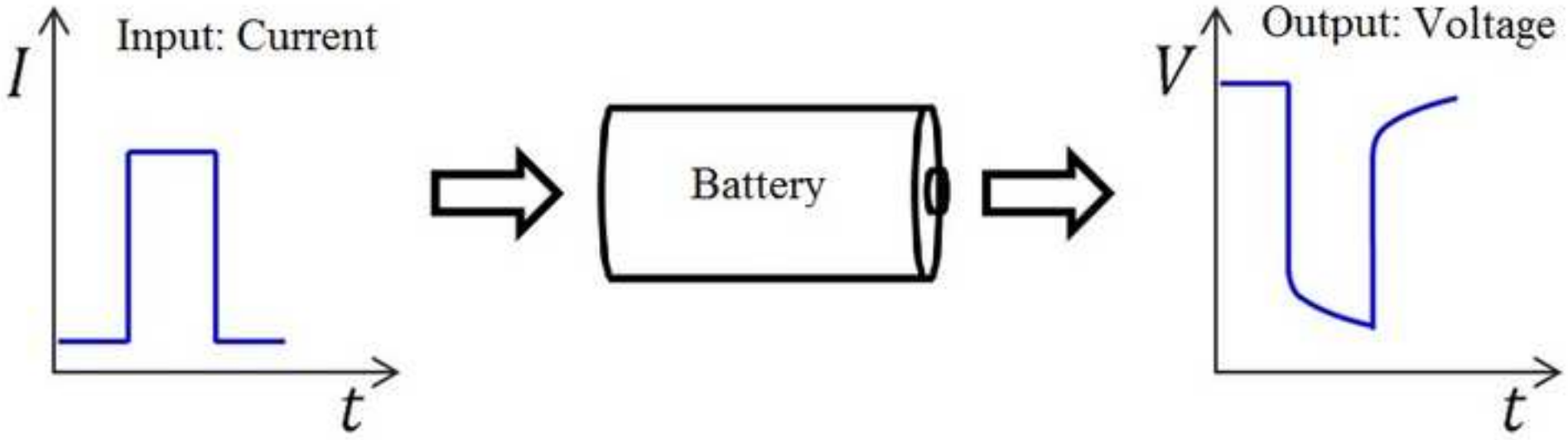

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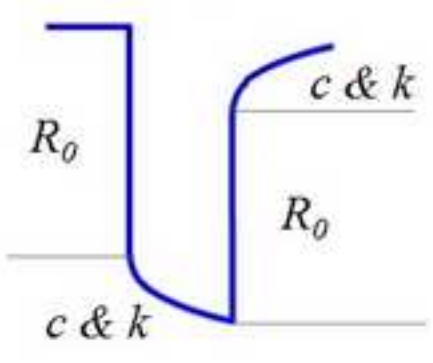
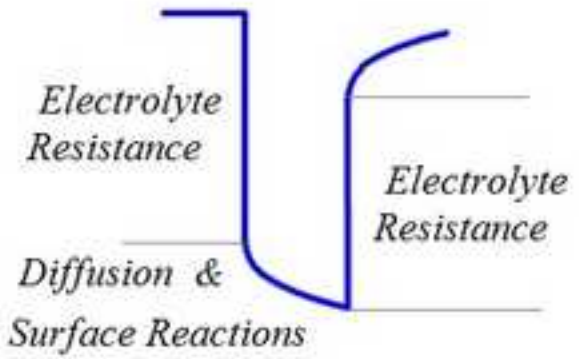
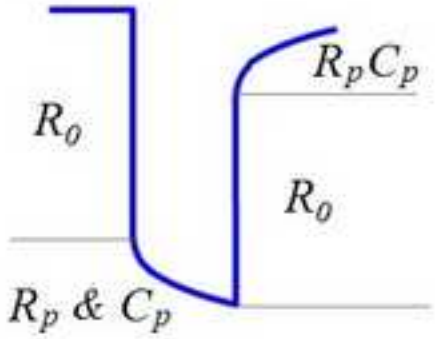


(a) Kinetic Battery Model (Mathematical Modelling)



(b) Electrochemical Modelling



(c) Electrical Circuit Modelling

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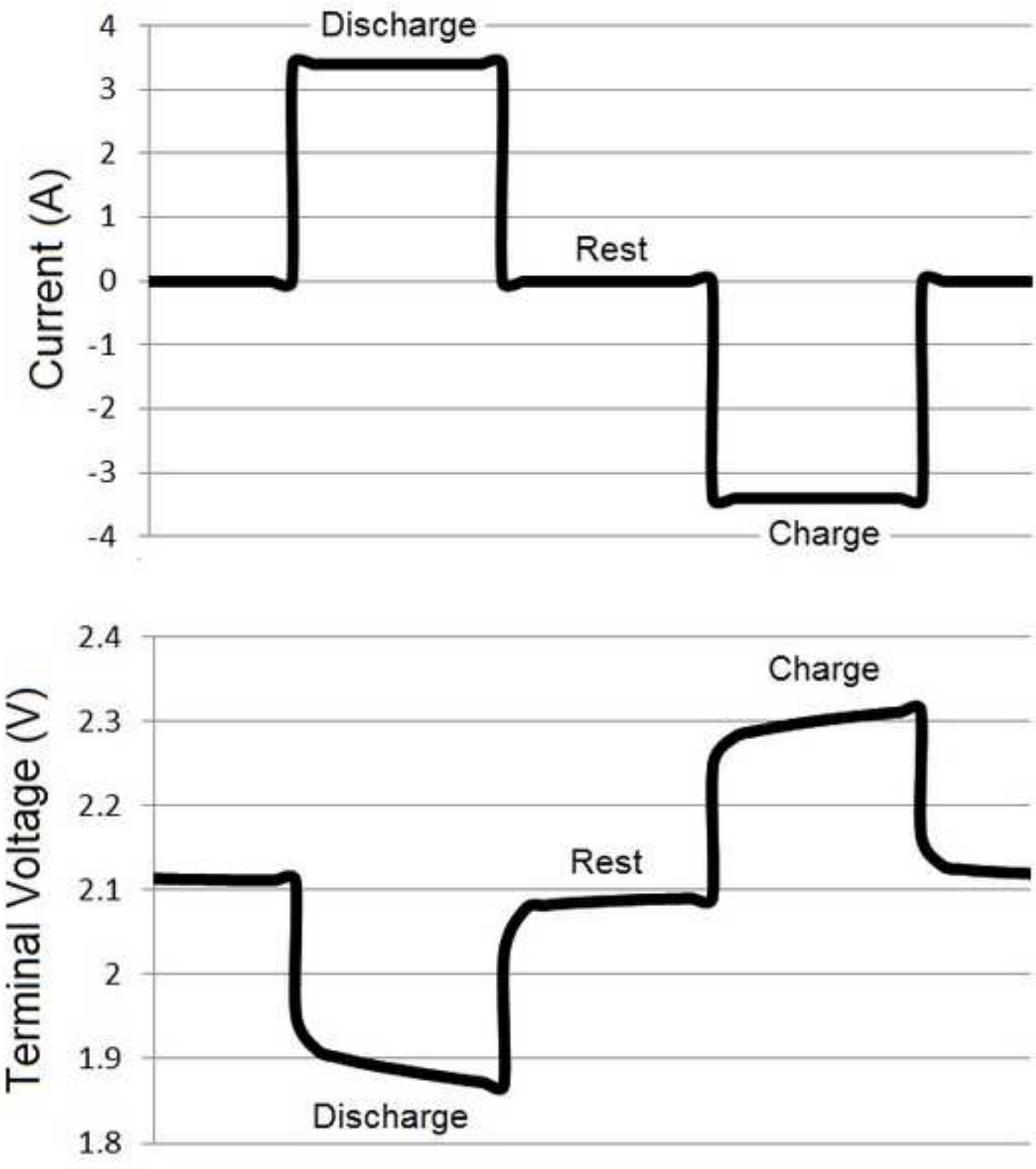

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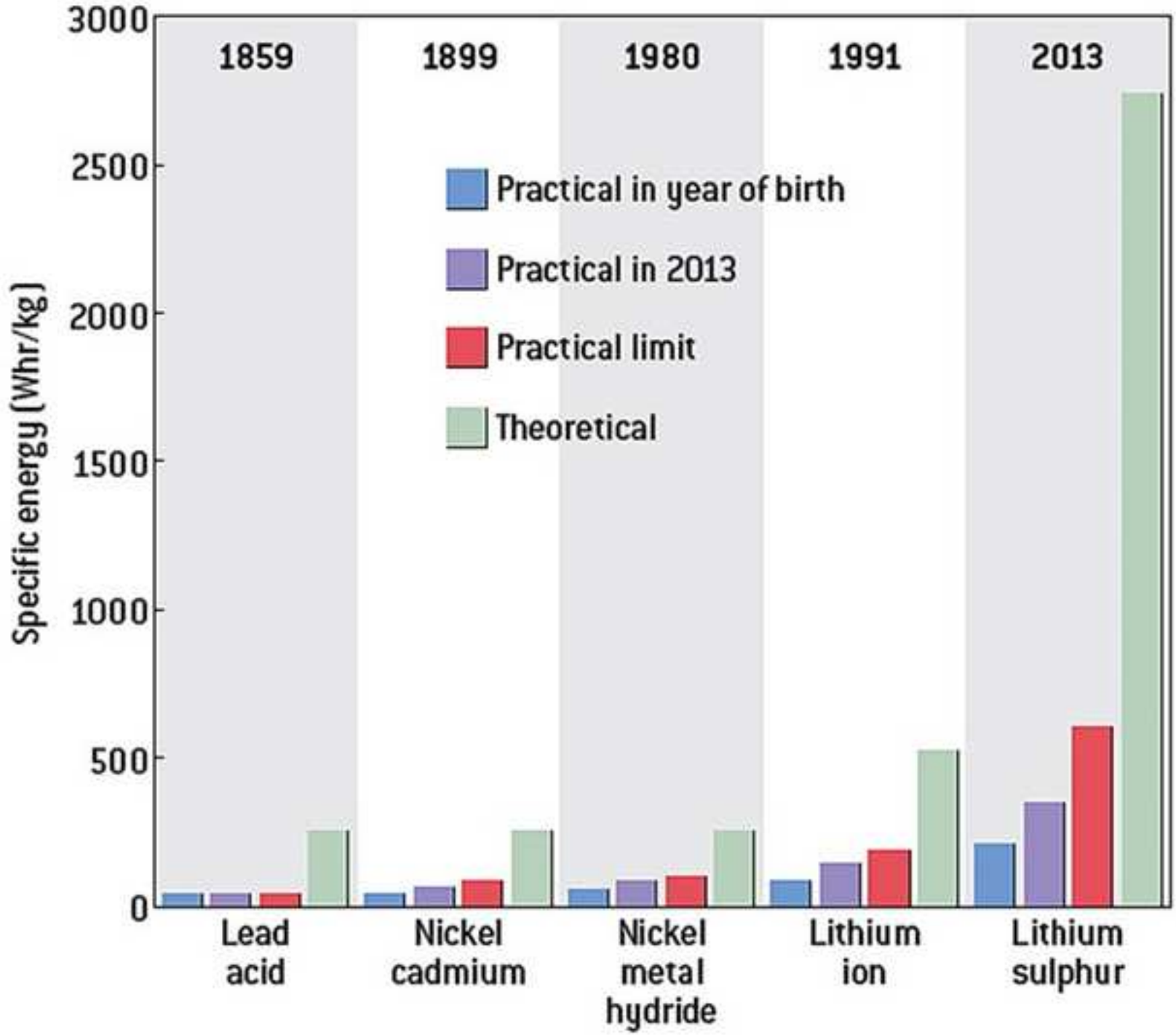

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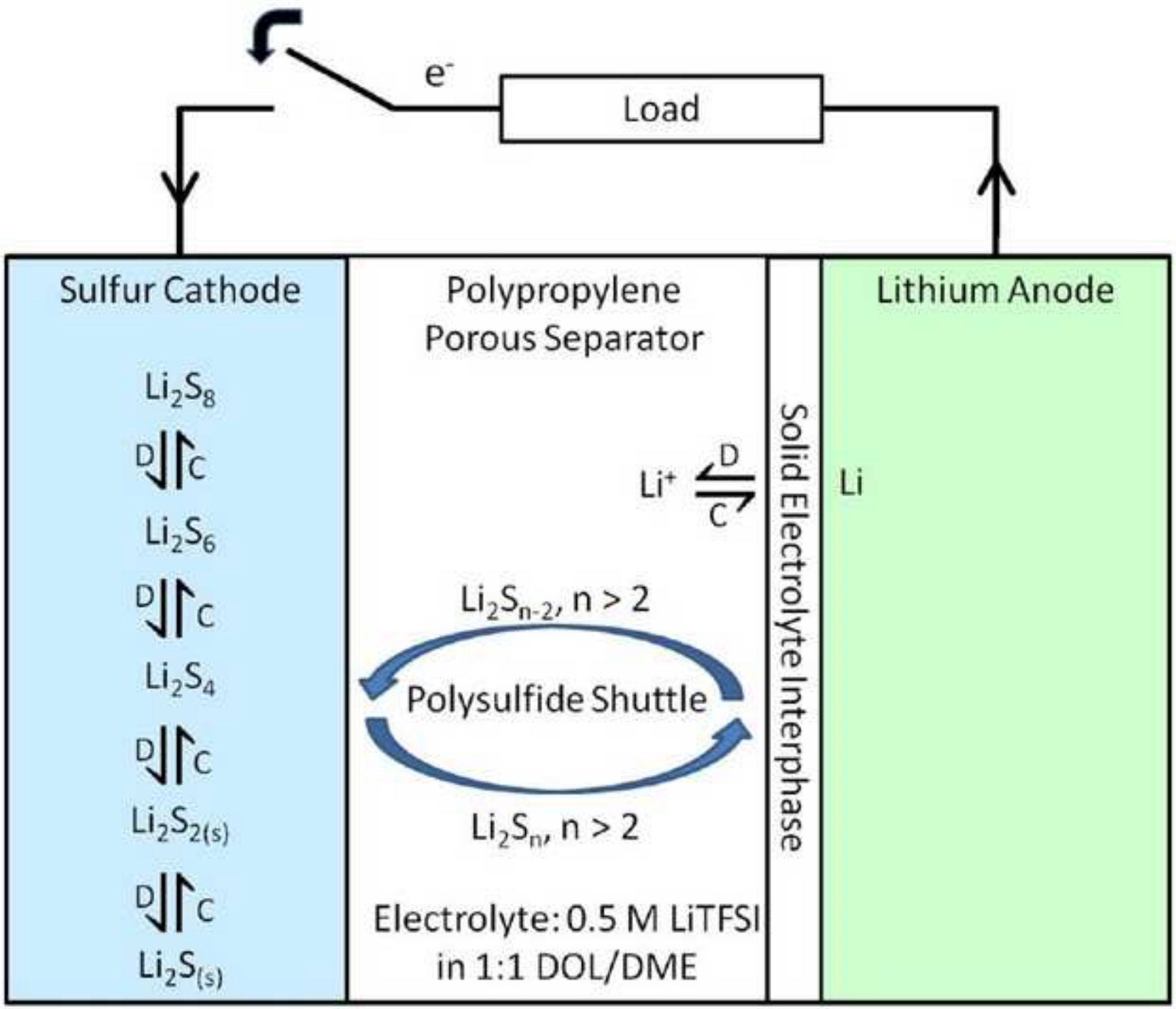

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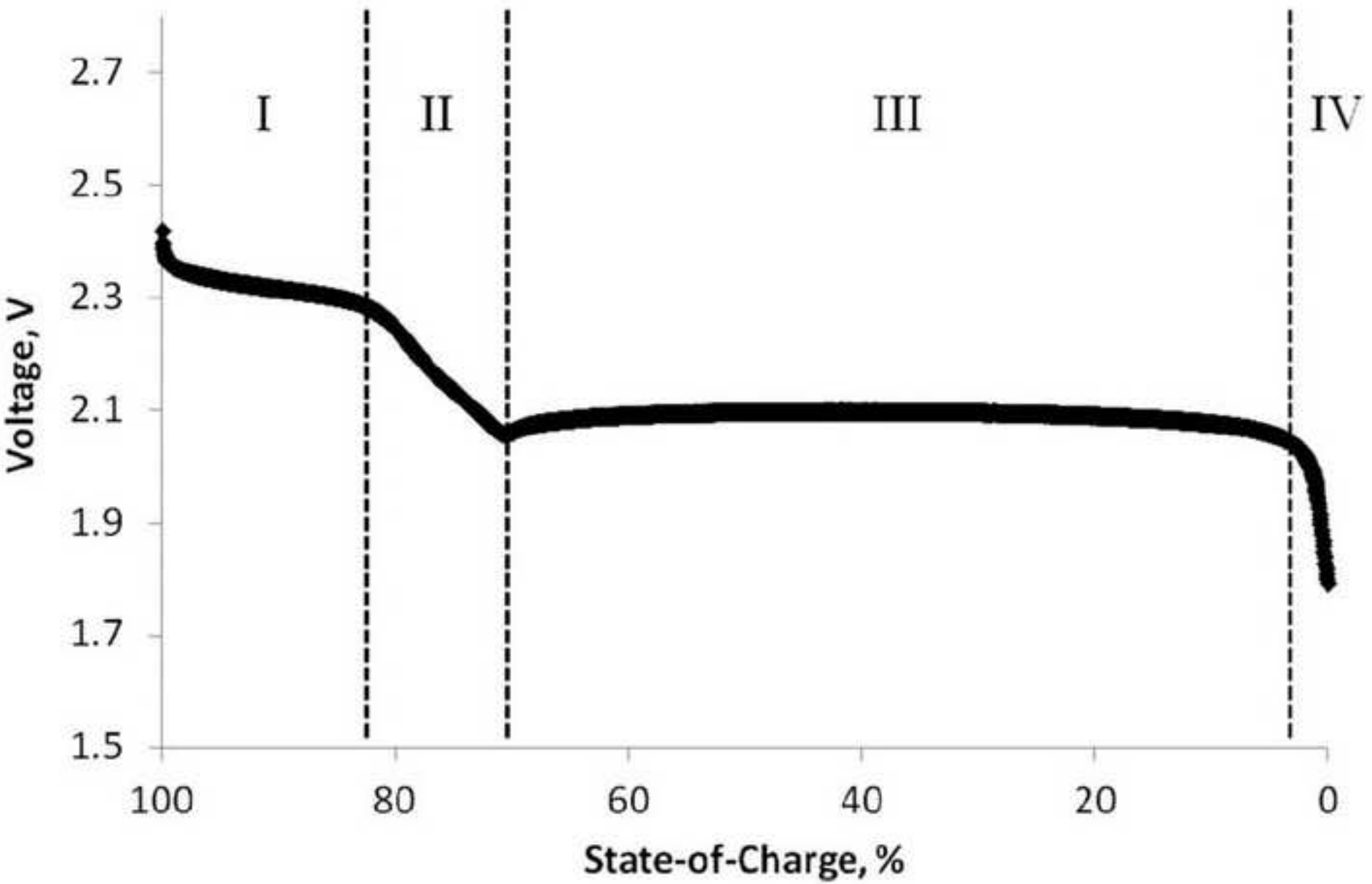

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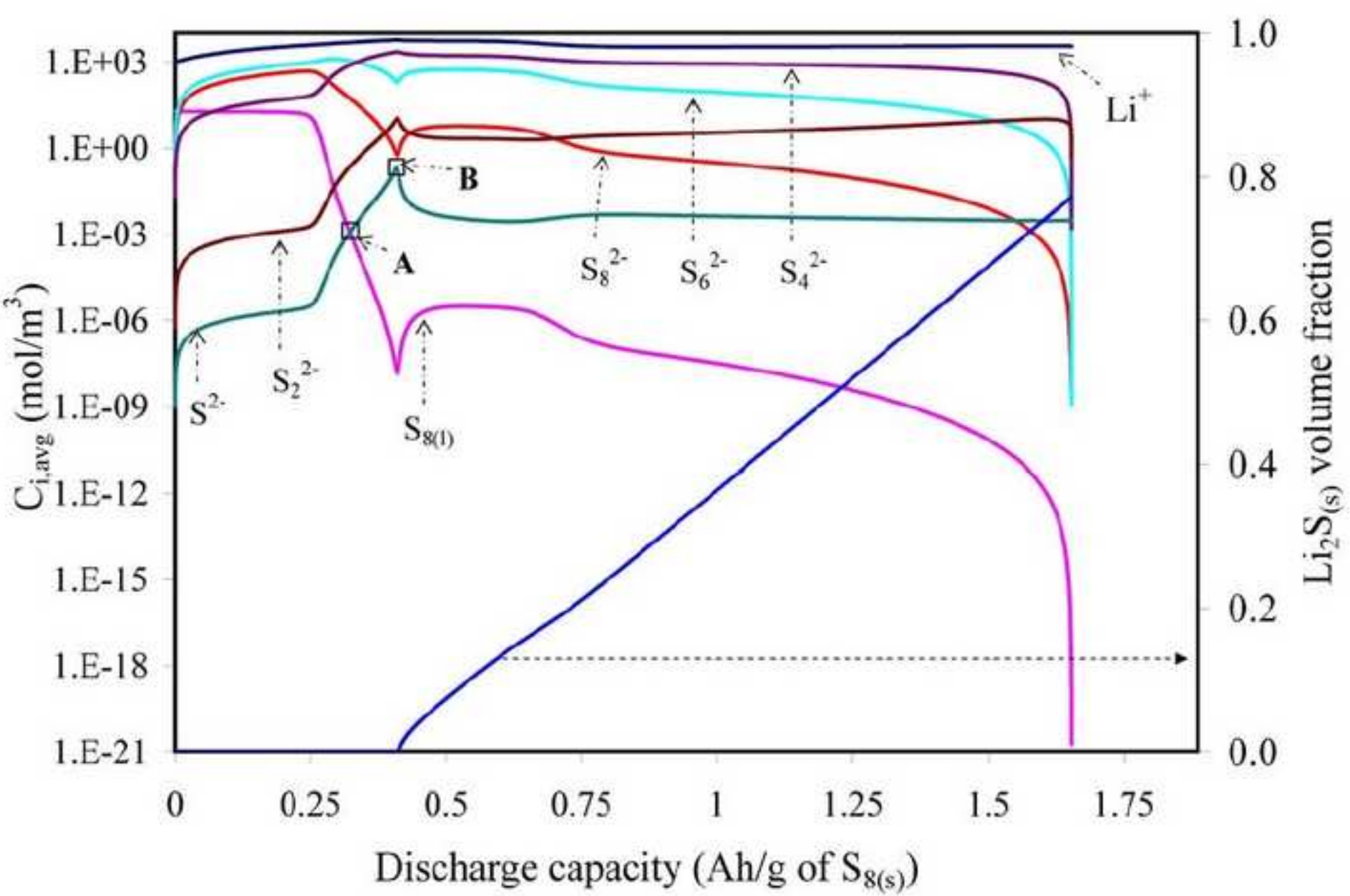

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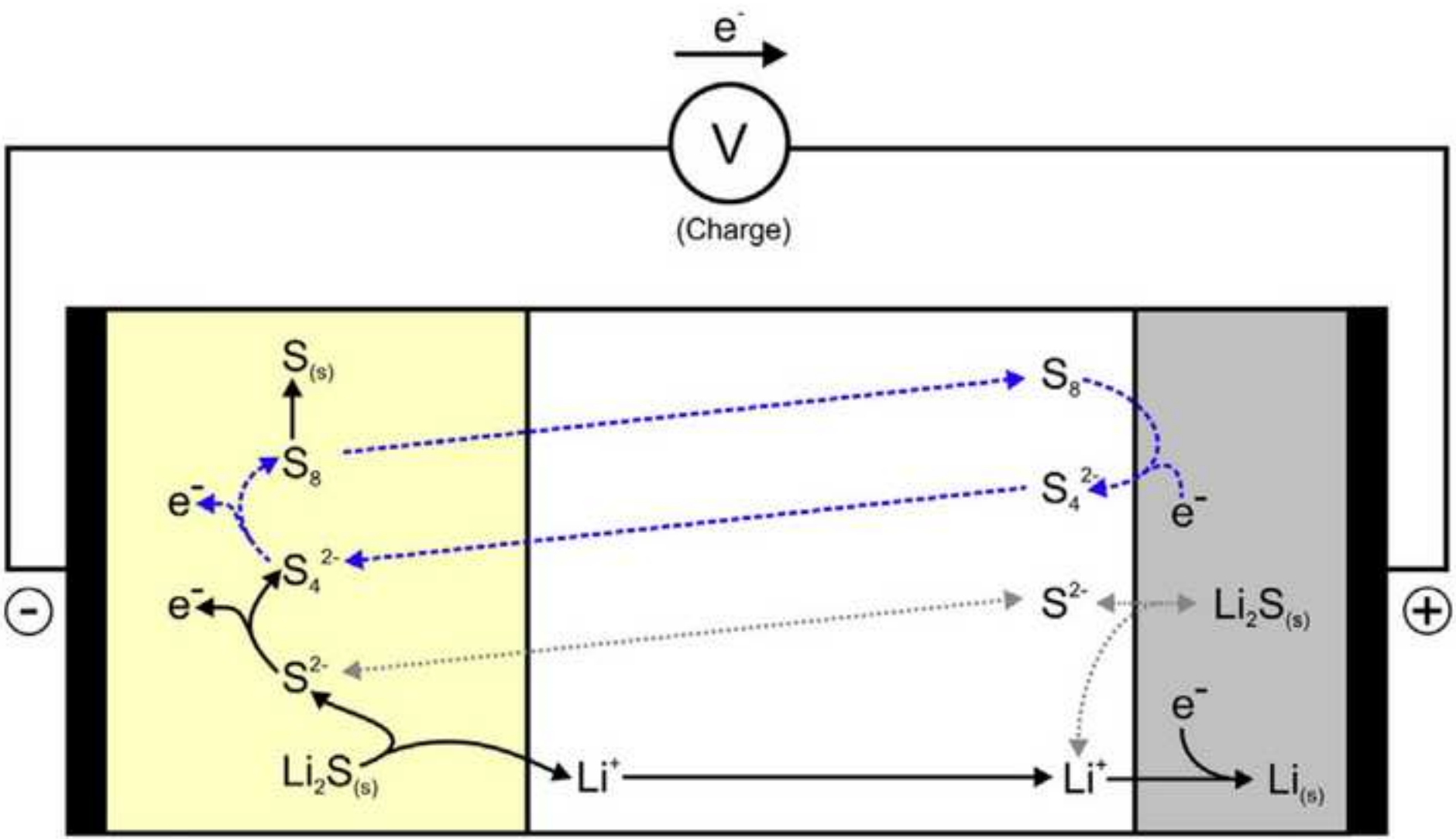

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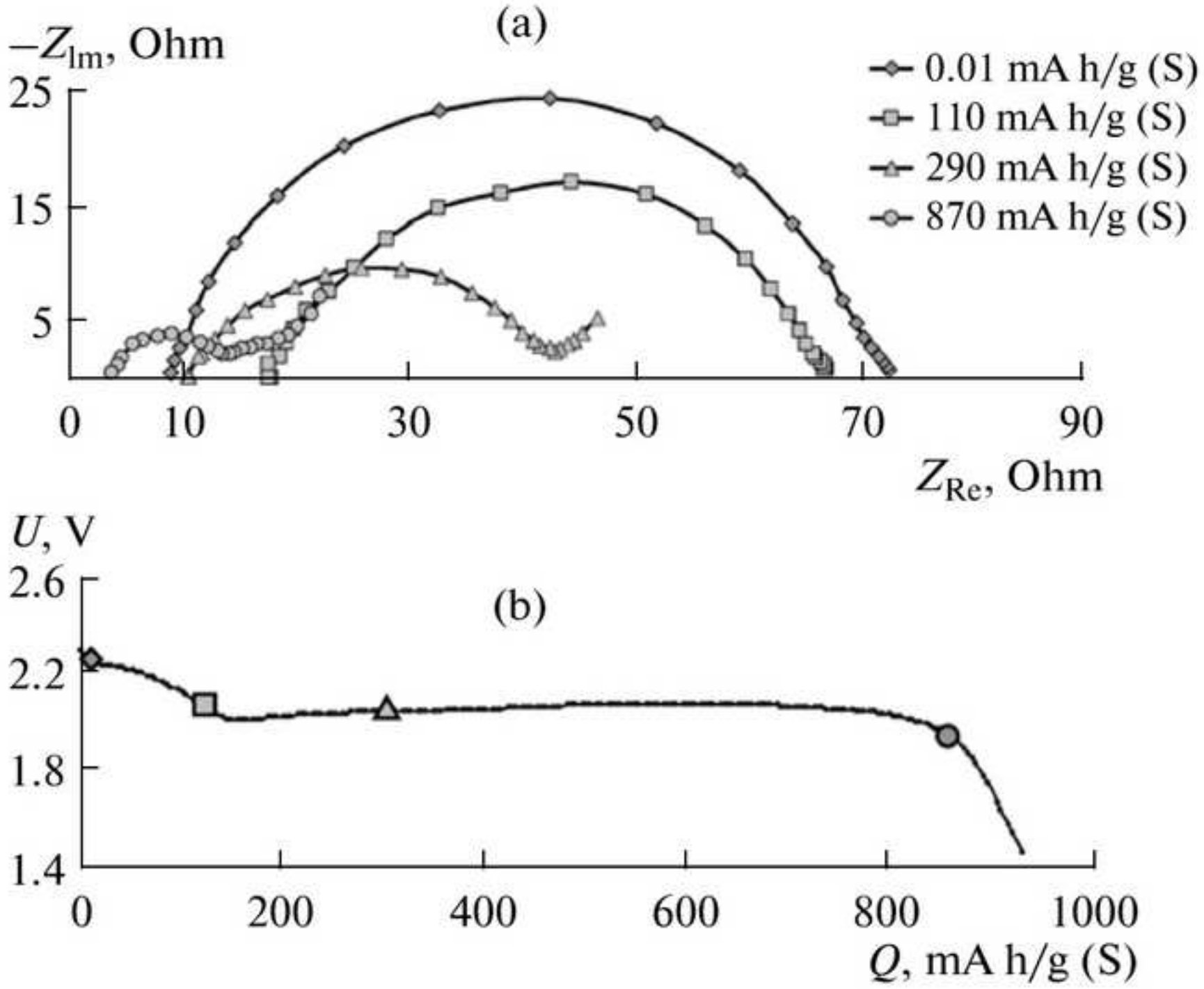

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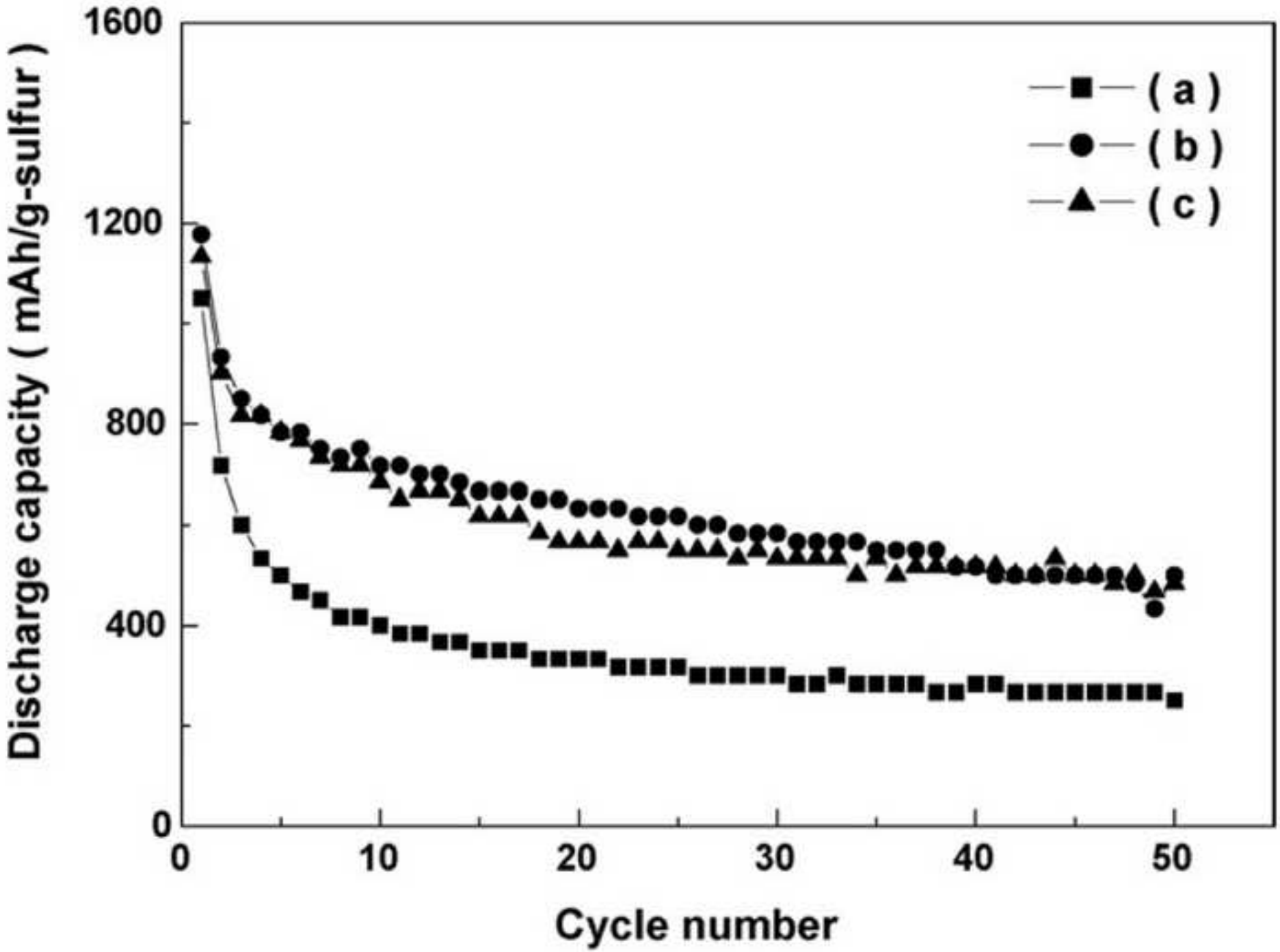

Table 1

Table 1: Different Li-ion battery packs manufacturers and EVs in which battery is used [11]

Cathode Material Types	EVs battery Packs Manufacturers	EVs Developers and EV Models	Battery Packs Usable Capacity (kWh)	Approx. Range under Normal Driving Conditions (miles)
Lithium Cobalt Oxide (LCO)	Panasonic, Tesla	Tesla-Roadster Daimler Benz-Smart EV	56 16.5	245 84
Lithium Manganese Oxide (LMO)	AESC, EnerDel, GS Yuasa, Hitachi, LG Chem, Toshiba	Think-Think EV Nissan-Leaf EV	23 24	99.4 105
Lithium Iron Phosphate (LFP)	A123, BYD, GS Yuasa, Lishem, Valence	BYD-E6 Mitsubishi-iMiEV	57 16	249 99.4
Lithium Nickle-Manganese-Cobalt Oxide (NMC)	Hitachi, LG Chem, Samsung	BMW-Mini E	35	150

Table 2

Table 2: Governing equations of a Li-ion cell electrochemical model [28]

Description	Equations and boundary conditions	
Charge		
Electrolyte phase	$\frac{\partial}{\partial x}\left(\kappa^{eff}\frac{\partial}{\partial x}\phi_e\right)+\frac{\partial}{\partial x}\left(\kappa_D{}^{eff}\frac{\partial}{\partial x}\ln c_e\right)+j^{Li}=0,\ \left.\frac{\partial\phi_e}{\partial x}\right\|_{x=0}=\left.\frac{\partial\phi_e}{\partial x}\right\|_{x=L}=0$	(3)
Solid phase	$\frac{\partial}{\partial x}\left(\sigma^{eff}\frac{\partial}{\partial x}\phi_s\right)-j^{Li}=0,\ \begin{cases}-\sigma_-^{eff}\left.\frac{\partial\phi_s}{\partial x}\right\|_{x=0}=-\sigma_+^{eff}\left.\frac{\partial\phi_s}{\partial x}\right\|_{x=L_-+L_{sep}+L_+}=\frac{I}{A}\\ \left.\frac{\partial\phi_s}{\partial x}\right\|_{x=L_-}=\left.\frac{\partial\phi_s}{\partial x}\right\|_{x=L_-+L_{sep}}=0\end{cases}$	(4)
Species		
Electrolyte phase	$\frac{\partial(\varepsilon_e c_e)}{\partial t}=\frac{\partial}{\partial x}\left(D_e^{eff}\frac{\partial}{\partial x}c_e\right)+\frac{1-t_+^0}{F}j^{Li},\ \left.\frac{\partial c_e}{\partial x}\right\|_{x=0}=\left.\frac{\partial c_e}{\partial x}\right\|_{x=L}=0$	(5)
Solid phase	$\frac{\partial c_s}{\partial t}=\frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_s}{\partial r}\right),\ \left.\frac{\partial c_s}{\partial r}\right\|_{r=0}=0,\quad D_s\left.\frac{\partial c_s}{\partial r}\right\|_{r=R_s}=-\frac{j^{Li}}{a_s F}$	(6)

Table 3

Table 3: Battery model discretization methods

Discretization method	**Description**	**References**
The Analytical Method	Finding an exact solution using analytical approaches such as the eigenfunction series expansion or the Laplace transform.	[49],[50]
Integral Approximation Method	Assuming a distribution across the cell for the distributed variable of interest and integrating the governing equations to convert the PDE to a single ODE.	[49],[51], [52],[53]
Padé Approximation Method	Approximating the transfer function that is obtained using the analytical method to desired order exponentials. In other words, Padé approximation is utilized to expand the infinitely differentiable hyperbolic functions in a power series at the origin.	[49],[54], [55],[56]
Finite Element Method	Approximating the response over subdomains and then developing transfer functions or state-space equations for the nodal dynamics.	[30],[49], [57],[58]
Finite Difference Method	Similar to the Finite Element Method with more simplicity but no convergence guarantee.	[26],[49], [58],[59], [60]
Ritz Method	Approximating the response by continuous functions over the whole domain such as Fourier series with the sinusoidal functions.	[49]

Table 4

Table 4: Li-ion cell parameters

A	cell surface area	R_{ct}	charge transfer resistance
a_S	specific interfacial surface area	R_f	contact resistance related to the physical connections
c_S	concentration of Li+ ions	R_S	particle radius
D_S	solid phase diffusion coefficient	U	equilibrium potential
F	Faraday's constant	$V(s)$	cell's terminal voltage
$I(s)$	Current	δ	thickness

Table 5

Table 5: Coefficients of the discretized transfer function

Coefficient	Value	Coefficient	Value
b_0	$\frac{495C_+\left[D_{S+}\right]^2}{AFa_{S+}\delta_+\left[R_{S+}\right]^5}$	a_0	0
b_1	$\frac{60C_+D_{S+}}{AFa_{S+}\delta_+\left[R_{S+}\right]^3}$	a_1	$\frac{3465\left[D_{S+}\right]^2}{\left[R_{S+}\right]^4}$
b_2	$\frac{C_+}{AFa_{S+}\delta_+R_{S+}}$	a_2	$\frac{189D_{S+}}{\left[R_{S+}\right]^2}$
d_0	$\frac{495C_-\left[D_{S-}\right]^2}{AFa_{S-}\delta_-\left[R_{S-}\right]^5}$	c_0	0
d_1	$\frac{60C_-D_{S-}}{AFa_{S-}\delta_-\left[R_{S-}\right]^3}$	c_1	$\frac{3465\left[D_{S-}\right]^2}{\left[R_{S-}\right]^4}$
d_2	$\frac{C_-}{AFa_{S-}\delta_-R_{S-}}$	c_2	$\frac{189D_{S-}}{\left[R_{S-}\right]^2}$

Table 6

Table 6: A summary of different battery model types, variables and parametrization techniques in the literature

Reference	Model Variables	Model type	Parameterization technique
[67]	SOC	Look-up table	Recursive Least-Squares
[70]	SOC	Polynomial functions	Unspecified
[71]	SOC, Temperature	Polynomial functions	Extended Kalman Filter
[43]	SOC, Temperature, Rate of current	Polynomial functions	Electrochemical Impedance Spectroscopy
[72]	SOC, Temperature, Rate of current	Polynomial functions	Unspecified
[74]	SOC, Temperature, Rate of current, SOH	Unspecified	Extended Kalman Filter
[75]	SOC, Temperature, Rate of current, SOH	Polynomial functions and correction factors	Unspecified
[76]	SOC, Temperature, Rate of current, SOH	Polynomial functions	Unspecified

Table 7

Table 7: Reactions in Li-S cell model during discharging [83]

Reaction	**Description**
$Li \rightleftarrows Li^{+} + e^{-}$	Oxidation at anode
$\frac{1}{2} S_{8(l)} + e^{-} \rightleftarrows \frac{1}{2} S_8^{2-}$ $\frac{3}{2} S_8^{2-} + e^{-} \rightleftarrows 2 S_6^{2-}$ $S_6^{2-} + e^{-} \rightleftarrows \frac{3}{2} S_4^{2-}$ $\frac{1}{2} S_4^{2-} + e^{-} \rightleftarrows S_2^{2-}$ $\frac{1}{2} S_2^{2-} + e^{-} \rightleftarrows S^{2-}$	Reduction at cathode
$S_{8(l)} \rightleftarrows S_{8(s)}$	Dissolution of Sulfur
$2Li^{+} + S_8^{2-} \rightleftarrows Li_2S_{8(s)}$ $2Li^{+} + S_4^{2-} \rightleftarrows Li_2S_{4(s)}$ $2Li^{+} + S_2^{2-} \rightleftarrows Li_2S_{2(s)}$ $2Li^{+} + S^{2-} \rightleftarrows Li_2S_{(s)}$	Precipitation of Lithium Sulfides

2015-12-29

A review on electric vehicle battery þÿ m o d e l l i n g : f r o m l i t h i u m - i o n t o

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