Electrochemical, AC impedance spectroscopy and cycling dynamic methods for the integrated extraction and characterization of lithium batteries

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In this study, a bridge between macroscopic measurements, such as AC impedance spectroscopy [1] and cycling dynamic methods [2], and electrochemical models [3] relying on microscopic models is further developed and explored for potential improvements and applications. A newly unified method is applied to extract the macroscopic model of batteries in general and then employ them in electrochemical models. The macroscopic aspect may find relationships that the electrochemical models have not yet taken into account, i.e., lithium ion saturation at the cathode/anode under different cycling and operating conditions. In addition, the proposed macroscopic and microscopic bridge may further serve for reverse engineering or improvement of the electrolyte with existing or alternative ones by performing molecular dynamics or creating new design iterations with experimental data.

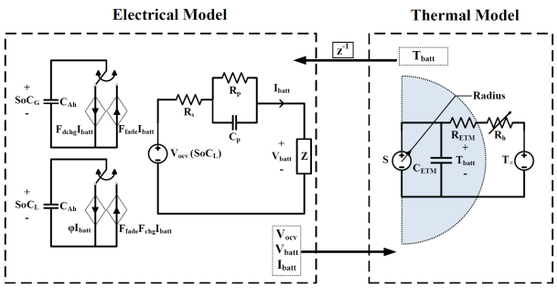

Figure 1 Advanced equivalent electrical and thermal integrated model for high power batteries

Figure 1 shows the proposed macroscopic equivalent integrated battery model and represents the most advanced and accurate model to date, which is fully dependent on the operating temperature and charging/discharging current. The addition of two state of charge calculators separate the global state of charge, SoC_G and the local state of charge, SoC_L ; where the former is a measure of how much Li may be ideally let to react with the active electrode materials while the latter is a measure of how much Li is locally allowed to react. R_s represents the interfacial resistance between the electrolyte and electrodes, R_p and C_p are directly proportional to the ionic conductivity of the electrolyte and represent the transient behavior of the losses. The open circuit voltage, V_{ocv} , is measured experimentally with respect to the calculated local state of charge, SoC_L .

In order to build the macroscopic and microscopic bridge, the electrochemical model is chosen to employ physical dimensions in order to emulate the transient phenomena observed during full sized battery conditions in extreme operations. The electrochemical model will employ (i) the potential in the solid electrolyte, (ii) the potential in the electrolyte, (iii) the transport in the electrolyte, (iv) the transport of lithium ions in the electrode material, (v) the conservation of charge and (vi) the Butler-Volmer equation. Its inputs will include temperature and the demanded/applied current.

Molecular dynamics can be employed to obtain electronic conductivities of different electrolytes. Two optimized geometries are shown in Figure 2 (a) and the simulation results of their respective conductivities are shown in Figure 2 (b). It will also be investigated if macroscopic models could estimate microscopic phenomena. Both the dynamic cycling and AC impedance methods are employed to obtain an equivalent circuit; advantages and disadvantages will be discussed. Having the macroscopic model, it will then be imperative to obtain (i) the V_{ocv} and (ii) the ionic conductivity of the battery. In addition, it will be discussed how to relate local lithium ion saturation to the Li concentration at the electrodes numerically.

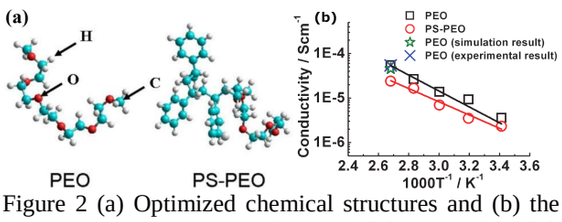

Figure 2 (a) Optimized chemical structures and (b) the Arrhenius relationship of the PEO and PS-PEO separators [4]

Figure 3 (left) shows initial results with a dimensionless temperature based model for a $LiMn_2O_4$ cathode battery. Finally, a convenient representation of the electrical and thermal properties of a battery is proposed, as seen in Figure 3 (right), where a $LiFePO_4$ cathode type battery is conveniently represented; it shows concentration discharge accelerators F_{disch} , equivalent thermal model properties embedded in normalized terms (*ETM* subscripts), and other important properties.

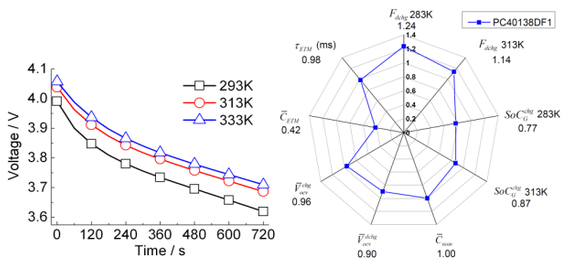

Figure 3 (left) Voltage changes with simulation time in different operation temperature for a dimensionless $LiMn_2O_4$ cathode battery and (right) a performance index chart for a $LiFePO_4$ battery

References

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