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A Modified Multiphysics model for Lithium-Ion batteries with a $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode

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ABSTRACT

Lithium-Ion Batteries lack performance and are costly for applications such as electric vehicles and electric energy storage systems. Multiphysics based battery models are one of the engineering tools to enhance their performance. In this regard, simulations have not only to provide qualitative but also quantitative valuable information. Our work focuses on the characterization and modelling of $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ based cells which has not been fully addressed yet. First, we present a modified multiphysics model compared to the conventional porous electrode theory for simulating these type of cells. The correspondence with experimental results is satisfactory but the model fails to accurately predict the voltage drop at high current rates.

1. Introduction

Today, the largest portion of primary energy consumption is transportation (31.8% in 2012 in the EU-28), a sector which depends almost exclusively on petroleum. While the need for individual transport continues to increase, emissions from internal combustion engines are contributing to air pollution and global warming [1]. With (Hybrid) Electric Vehicles ((H)EV) recharged by electricity coming from renewable energy, air pollution and dependence on petroleum can be reduced dramatically. As one of the costliest and heaviest components of the electric propulsion system, the battery is still a bottleneck hindering the breakthrough of (H)EVs [2]. In the battery industry development and optimization is done by build and break cycles. As a consequence battery development is an extremely time consuming process. In many other areas software is used during the expert analysis phase [3,4]. The ability to use software based on electrochemical or multiphysics models to design and test could speed up the process significantly [5].

We will look into models describing Li-Ion Batteries (LIBs) on a macroscopic level, meaning that matter and its properties are considered as a continuum. In practice it is very cost and time consuming to solve numerically the continuum equations describing the dynamics of a battery cell in all detail over a complete discharge [6,7]. Not only the three-dimensional structure is complex but many material parameters are not exactly known and change during (dis)charge. Hence many assumptions are made to simplify the mathematical description of LIBs. The commonly used model of Newman [8] includes multiple simplifications: the solvent is treated as one species, the exact three-dimensional morphology is omitted by averaging the equations out over the porous media and only one characteristic diffusion length is used for the particles constituting the electrodes. This model allows to simulate current-voltage curves notwithstanding the fact that certain material and design parameters are not (well) known. Always some sort of fitting with experimental results has to be done [9,10]. Many authors have simplified or extended Newman's model. In reference [9] the researchers focus on the volume-averaging technique. A so called micro-macroscopic model was developed to incorporate the detailed morphology of the electrode/electrolyte interface. Darling [11] was the first who considered parasitic side reactions which cause capacity loss of lithium manganese oxide based LIBs, Ramadass [12] continued his effort for lithium cobalt oxide based LIBs. Model extension is still ongoing. At the same time it is aimed to minimize the computational effort for instance by simplifying the diffusion equation in the solid phase [13–15]. Large efforts are focused on better assessing the impact of porosity and tortuosity of the electrodes and separator [16,6,7]. Other researchers are making progress by using phase-field modelling [17] to accurate describe phase changing materials. Especially for simulating lithium iron phosphate electrodes these models seem very promising [18–20]. Others look at a better understanding and description of ionic transport near charged surfaces [21], transport of lithium ions in an intercalation host [22] and electrode kinetics of certain electrode materials [23].

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In this paper we present an enhanced multiphyscs model describing LIBs with a liquid electrolyte and two intercalation electrodes. Most LIB models on this scale consider the electrolyte to be a concentrated binary electrolyte. The framework presented here allows to consider more then three components such as multiple solvent species and/or additives, when the corresponding phenomenological coefficients are known. When the model is applied to a binary concentrated solution its equivalent to the description of a concentrated solution given in reference [24] and [25]. The advantage of our formulation is that transport is described by the salt concentration and potential. The current density is derived from ion-fluxes. By proceeding in this way an elegant set of equations is obtained were cause (gradients of concentration and potential) and effect (a net current flow) are separated. Then the model is validated by comparing experimental and simulated results for a lithium nickel manganese cobalt oxide-graphite based Li-Ion cell with a capacity of 18,7Ah per m^2 electrode. The optimization of the input parameters is first done by fitting simulation results to experimental results of the discharge profiles separately for each electrode material versus lithium metal. We have chosen graphite and $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, introduced by Ohzuku [26], respectively for the negative and positive electrode. Although this is a commercial and promising electrode combination, at the time of writing this text, no publications presenting simulation results based on a multiphysics model of this type were found. It is our goal to fill this gap which will lead to a better understanding of battery operation and degradation.

2. Model development

When a Li-Ion Battery (LIB) is discharged, lithium ions are transported from the bulk of the negative electrode to its interface with the electrolyte where they are transmitted into the electrolyte. Driven by differences in potential and concentration that arise, cations (Li^+) and anions (mostly PF_6^-) travel through the electrolyte. At the positive electrode lithium ions are transferred onto the host material where they move further into the crystal lattice of the active electrode material. The framework for describing these phenomena in LIBs at the macroscopic scale is that of non-equilibrium thermodynamics. We will first present the ion transport in the electrolyte. With physics-based models for LIBs a solid phase, representing the electrodes, and a liquid phase, representing the electrolyte, are distinguished.

2.1. Transport in concentrated solutions

Most commercial LIBs use lithium hexafluorophosphate dissolved in a mixture of organic esters such as ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) as an electrolyte [27]. The concentration of the salt is around 1mol/l. Dilute solution theory is not suited to deal with transport phenomena in such electrolytes. With ideal dilute solutions the flow of an ionic species is uninfluenced by the presence of other species. In concentrated solutions however the flow of an ionic species is affected by its own presence and by the that of the other species [25]. Additionally the higher proximity of different ions causes the transport properties to depend on the local composition. The framework to deal with these phenomena is that of non-equilibrium thermodynamics. The interested reader is referred to references [28] and [24] for more details. Here we will focus only to the definition of the phenomenological coefficients which play a prominent role in the derivation of the transport equations. Prior to any experience one can state that, each irreversible flux J_i depends upon all K thermodynamic driving forces, X_j ([24,29]):

$$J_i = J_i\left(X_j\right) \tag{1}$$

For small deviations, this dependence can be linearized as

$$J_i = \sum_{j=1}^{K} L_{ij} X_j \tag{2}$$

Where L_{ij} are phenomenological coefficients. This general form includes for instance Fick's law of diffusion or Fourier's law of heat conduction. It also allows for cross-phenomena in which the presence of one species influences the flow of all the other species. When looking at mass fluxes in an isothermal system, we can postulate that the driving force for diffusion of component k is ([24])

$$\vec{X}_j = -\left[\vec{\nabla}\mu_j + z_j F \vec{\nabla}\Phi_e\right] \tag{3}$$

Where Φ_e is the potential in the electrolyte and μ_j is the chemical potential of species j.

To make this general expression applicable we have to relate variations in chemical potential to variations in concentrations. From thermodynamics we know that

$$\mu_j = \mu_j^0 + RT\ln f_j + RT\ln c_j \tag{4}$$

Where the activity coefficient f_j of species j depends on the pressure, temperature and concentration. The standard chemical potential μ_j^0 is only a function of the pressure and temperature which we assume constant. The irreversible mass fluxes in equation (2) can then be written as [29]

$$\vec{J}_i = -\sum_{j=1}^{I} \vec{\nabla}\cdot\left(D_{ij}\vec{\nabla}c_j\right) - \vec{\nabla}\cdot\left(\omega_i \vec{\nabla}\Phi_e\right) \tag{5}$$

Where we have introduced the diffusion coefficients

$$D_{ij} = RT\left(\frac{L_{ij}}{c_j} + \sum_{l=2}^{I} L_{il}\frac{\partial \ln f_l}{\partial c_j}\right) \tag{6}$$

and the mobility's

$$\omega_i = F\sum_{l=2}^{I} z_l L_{il} \tag{7}$$

With I the number of components contained in the electrolyte system. The K thermodynamic driving forces are limited to I for the irreversible fluxes under consideration. Equations (5) to (7) are applicable to describe the transport in a concentrated electrolyte solution containing I species, applicable to LIBs. A common solution of $1 mol/l$ $LiPF_6$ in EC/DMC (50/50), not considering the additives, requires the knowledge of 6 ($\frac{I(I-1)}{2}$) phenomenological coefficients. When these coefficients are known this formulation allows to simulate fluxes of individual species making it possible to evaluate their effect. If they are unknown, which is the case today, it is convenient to consider the electrolytic solution as being a binary solution [27]. So the solvent mixture is treated as one component.

The ionization of a binary electrolyte can be written as

$$A_{\nu_-}B_{\nu_+} \rightleftharpoons \nu_- A^{z-} + \nu_+ B^{z+} \tag{8}$$

with A^{z-} representing the anion and B^{z+} representing the cation.

Choosing the solvent-fixed frame (i.e. $\vec{J}_1 = 0$) and given that the solvent is neutral and with chemical potential assumed to be constant, we can write the two independent mass fluxes of the cation and anion as

$$\vec{J}_+ = -D_{++}\vec{\nabla}c_+ - D_{+-}\vec{\nabla}c_- - \omega_+\vec{\nabla}\Phi_e \tag{9}$$

$$\vec{J}_- = -D_{-+}\vec{\nabla}c_+ - D_{--}\vec{\nabla}c_- - \omega_-\vec{\nabla}\Phi_e \tag{10}$$