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Mathematical model of lithium-ion batteries with blended-electrode system

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HIGHLIGHTS

- Two mathematical models of lithium-ion cell with blended-electrodes are developed.
- Equilibrium model can easily calculate equilibrium characteristics of a blended-electrode.
- Dynamic model can predict dynamic performance of a lithium-ion cell with blended-electrodes.
- Developed model is validated with experiment data and shows good agreements.

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ABSTRACT

Many lithium-ion batteries have electrodes made of multiple types of active materials in order to take advantage of each active material. According to the types and blending ratios of constituting active materials, there can be numerous combinations of blended-electrodes, resulting in different performance characteristics. This paper introduces how to numerically model lithium-ion batteries with blended-electrodes, and predict their performance. Further, this paper demonstrates how to apply the developed model to designing new batteries. First, we propose an equilibrium model which can predict equilibrium characteristics of a blended-electrode. Second, a physics-based lithium-ion cell model with blended-electrodes is proposed. Developed model is validated with experimental data and shows good agreements.

1. Introduction

Although lithium-ion batteries commercialized by SONY have several merits such as larger capacity, lighter weight, and good coulombic efficiency compared to previously used batteries of other chemistry such as nickel-metal hydride batteries, there has been doubt that lithium-ion battery is not safe enough to be used for automotive power source. However, recently, lithium-ion battery is getting much more public, industrial attention. Several automakers have launched hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and battery electric vehicles (BEV) powered by lithium-ion batteries after GM successfully launched the first commercialized plug-in hybrid vehicle, VOLT™ which loads LG Chem's high performance lithium-ion batteries. In contrast to small batteries for portable electronics, automotive lithium-ion batteries must sustain severe operating conditions and requirements. Therefore, it requires much more time and efforts to develop large-formatted automotive batteries than small batteries for mobile applications.

Typical lithium-ion batteries are composed of negative active materials, positive active materials, electrolyte, separator, additives, and current collectors. Active materials are the most important among them since they determine power and energy of a battery. Many negative and positive active materials have been searched up to now and each of active material has its own characteristics such as operating potential profile, capacity and power. For example, $LiMn_2O_4$ has good rate capability and high power with relatively low cost and less safety problem. But, it shows low capacity and Manganese (Mn) dissolution problem also. In contrast, Li(Ni, Mn, Co)O_2 has more capacity compared to $LiMn_2O_4$, but shows lower power due to the layered structure and lower operating potential window. Olivine material such as $LiFePO_4$ is considered as one of promising positive materials due to low cost, improved safety with large capacity. Many researches to overcome low electronic

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conductivity and very low lithium diffusion rate of $LiFePO_4$ (briefly 'LFP') particle have been conducted [1–4]. As briefly listed above, most of active material have both merits and demerits together. Therefore, it is important to select proper active materials for specified purposes. Since large battery capacity is the most important factor for full electric vehicles (EV), $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (briefly 'NMC') can be selected as positive active material and graphite can be used for negative electrode. In contrast, high power is the most required quality for hybrid electric cars (HEV). In this case, spinel materials such as $LiMn_2O_4$ (briefly 'LMO') and amorphous materials such as carbon can be adopted for positive electrode and negative electrode, respectively. When both capacity and power are important, multiple active materials can be blended together, so called 'blended-electrode'.

Several papers about experimental work on blended-electrodes have been published. Mitigating Manganese dissolution and improving capacity retention by blending different active materials together were considered important by several researchers [5–7]. Fergus [8] extensively reviewed cathode materials including composite electrodes. He categorized electrode with different mixed particles and electrodes with coated particles layered as composite electrode. Whitacre et al. [9] constructed fully mixed (blended) electrodes, fully segregated electrodes and layered electrodes by using $LiFePO_4$ and $Li(Li_{0.17}Mn_{0.58}Ni_{0.25})O_2$. They tried to take advantages of composite electrode from each active material (high rate capability of $LiFePO_4$ and large capacity of $Li(Li_{0.17}Mn_{0.58}Ni_{0.25})O_2$ and they found that segregated active material configuration is the most promising solution with those two active materials.

As briefly reviewed above, it is worthwhile to consider blending several active materials together to improve cell performance. However, blending different active materials may cause some problems in a complex slurry mixing process or electrode coating process, which may result in increased manufacturing cost. In addition, much time and cost would be required to find optimum blending ratio for target performance of a cell. Actually, it takes much time and cost to finalize cell chemistry because cell makers go through several screening tests for candidate materials. Further, numerous new active materials are being introduced by material makers. Although, it is good for cell makers to have many options to choose, required time and cost for a new cell development may increase as the combination number of materials grows larger. If the performance of a new cell with blended-electrodes can be mathematically predicted before the actual cell is constructed, cell development cost will be significantly saved.

Few publications about modeling work on blended electrodes can be found up to now. Darling and Newman [10] started a modeling work on the electrode with two distinct particle sizes. Gomadam et al. [11] developed a mathematical model simulating a composite electrode made of carbon monofluoride (CF_x) and silver vanadium oxide (SVO) for medical applications. Although their model is relatively simplified with many assumptions, their modeling result showed good agreement with the experimental result from a small half cell test within moderate C-rate discharging condition. Albertus et al. [15–17] conducted more extensive modeling work on blended electrodes. They modified their mathematical cell model to treat electrodes made of multiple types of active particles, and simulated several composition of two types of active materials ($LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ and $LiMn_2O_4$). They presented that their blended electrode showed combined characteristics (such as power and energy) of each pure active material. Jung and Kang [18] introduced a multi-dimensional model of lithium-ion cells with blended-electrodes. But, their model was an empirical model which could not be used to predict characteristics of a lithium-ion cell without actual experiment data.

This paper introduces how to predict performance of lithium-ion batteries with blended-electrodes by mathematical method. First, we introduce the blended-electrode model in equilibrium state, which is useful to predict open-circuit voltage of a blended-electrode with arbitrary combinations of multiple active materials. Second, the physics-based dynamic model is explained, which can simulate battery performance in dynamic operating conditions and explain physico-chemical phenomena inside blended-electrodes.

2. Equilibrium model

A pure active material has a distinct equilibrium voltage profile according to lithium intercalation level or lithium stoichiometry, which can be used for us to predict charging/discharging characteristics of a cell made of the active material. By combining such equilibrium voltage data of several active materials, it is possible to predict basic characteristics such as discharging profile of a blended-electrode as follows.

Fig. 1 represents equilibrium voltage profiles of basic active materials for this study. The basic concept of the present equilibrium model of a blended-electrode is that the blended-electrode is in thermodynamically equilibrium state. In other words, the surface energy level (or the potential) of the constituting active particles should remain same level by minimizing potential difference between active particles. This causes each different active particle may have different state of charge (lithium stoichiometry) under equilibrium condition of the blended-electrode. Therefore, we can find out state of charge (lithium stoichiometry) of each constituting active material. Theoretical capacity of $LiMn_2O_4$ is about 150 mAh g^{-1} while usable capacity is about 107 mAh g^{-1} (150–107 = 43 mAh g^{-1} is reserved to protect the crystal structure). Therefore, minimum lithium stoichiometry (soc 100%) of $LiMn_2O_4$ is $stoich_{100} = 1.0 - 107/150 = 0.287$ and maximum lithium stoichiometry (soc 0%) is $stoich_0 = 1.0$ when irreversible loss is ignored. So, we can setup following functions using Fig. 1 with above relation.

$$U_i \begin{cases} = f_1(capa_i) \\ = f_2(stoich_i) \\ = f_3(soc_i) \end{cases} \quad \text{where} \quad \begin{cases} stoich_i = \dfrac{capa_i}{capa_{max,i}} \\ soc_i = \dfrac{stoich_i - stoich_{0,i}}{stoich_{100,i} - stoich_{0,i}} \end{cases} \tag{1}$$

Inversely, lithium stoichiometry or SOC can be found for the given equilibrium potential also by transforming the above functions as follows:

$$\begin{cases} f_1^{-1}(U_i) = capa_i \\ f_2^{-1}(U_i) = stoich_i = \dfrac{capa_i}{capa_{max,i}} = \dfrac{f_1^{-1}(U_i)}{capa_{max,i}} \\ f_3^{-1}(U_i) = soc_i = \dfrac{stoich_i - stoich_{0,i}}{stoich_{100,i} - stoich_{0,i}} = \dfrac{f_2^{-1}(U_i) - stoich_{0,i}}{stoich_{100,i} - stoich_{0,i}} \end{cases} \tag{2}$$

Note that the maximum capacity($capa_{max}$), the minimum lithium-stoichiometry ($stoich_0$), and the maximum lithium-stoichiometry($stoich_{100}$) of the active material i are known values. In order to get a full voltage profile of a blended-electrode with n-constituting active materials, we calculate accumulated capacity, lithium stoichiometry, and SOC of each material while sweeping equilibrium potential from U_{max} to U_{min} as follows: