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Review

A review of blended cathode materials for use in Li-ion batteries

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HIGHLIGHTS

- This review surveys the up to date literature advances.
- Unique advantages of blended materials are listed.
- Challenges to existing materials and future directions are covered.
- Review provides important status update of the blended materials.

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ABSTRACT

Several commercial automotive battery suppliers have developed lithium ion cells which use cathodes that consist of a mixture of two different active materials. This approach is intended to take advantage of the unique properties of each material and optimize the performance of the battery with respect to the automotive operating requirements. Certain cathode materials have high coulombic capacity and good cycling characteristics, but are costly and exhibit poor thermal stability (e.g., $LiNi_xCo_{1-x-y}Al_yO_2$). Alternately, other cathode materials exhibit good thermal stability, high voltage and high rate capability, but have low capacity (e.g., $LiMn_2O_4$). By blending two cathode materials the shortcomings of the parent materials could be minimized and the resultant blend can be tailored to have a higher energy or power density coupled with enhanced stability and lower cost. In this review, we survey the developing field of blended cathode materials from a new perspective. Targeting a range of cathode materials, we survey the advances in the field in the current review. Limitations, such as capacity decay due to metal dissolution are also discussed, as well as how the appropriate balance of characteristics of the blended materials can be optimized for hybrid- and electric-vehicle applications.

1. Introduction

1.1. Motivations for blending cathode materials

There is an intense interest in the battery industry to identify ways to improve the cathodes[1] used in Li-ion batteries for automotive-propulsion applications in terms of energy, power, safety, life, and cost. Blending cathode materials [1–11] is a new approach to designing better batteries for hybrid electric, plug-in hybrid electric, and battery electric vehicles (HEVs, PHEVs, and BEVs, respectively). The active material for a 'blended' cathode is comprised of a physical mixture of two or more distinct lithium intercalation compounds.[2] The motivation for blending these compounds is to achieve a more balanced performance compared to what is possible with any individual compound. For example, in a blended cathode system composed of $LiMn_2O_4$ (LMO, also referred to as "spinel"[3]) and $LiNi_xCo_{1-x-y}Al_yO_2$ (NCA), the NCA has a higher capacity ($\sim$195 mAh g^{-1}) and is more chemically stable (i.e., life); but its thermal stability is inferior. Alternatively, spinel has a higher operating voltage and better rate capability and is less costly. Because many of the shortcomings of spinel are favorable attributes of NCA, blending these two materials has received considerable attention [2]. Although the NCA/spinel blend may have less desirable storage life than pure NCA, the cost, energy, power and safety

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[1] In this review we use the term "cathode" to refer to the positive electrode and anode refers to the negative electrode, although in rechargeable batteries the positive electrode is an anode on charge.

[2] In the scanning electron micrograph shown in Fig. 2(a) (Ref. [2]), the two distinct materials of which this blended cathode is fabricated can be readily discerned.

[3] Although the term "spinel" generally refers to a type of chemical structure, we use the term to refer to the lithium–manganese-oxide spinel compound $Li_xMn_2O_4$.

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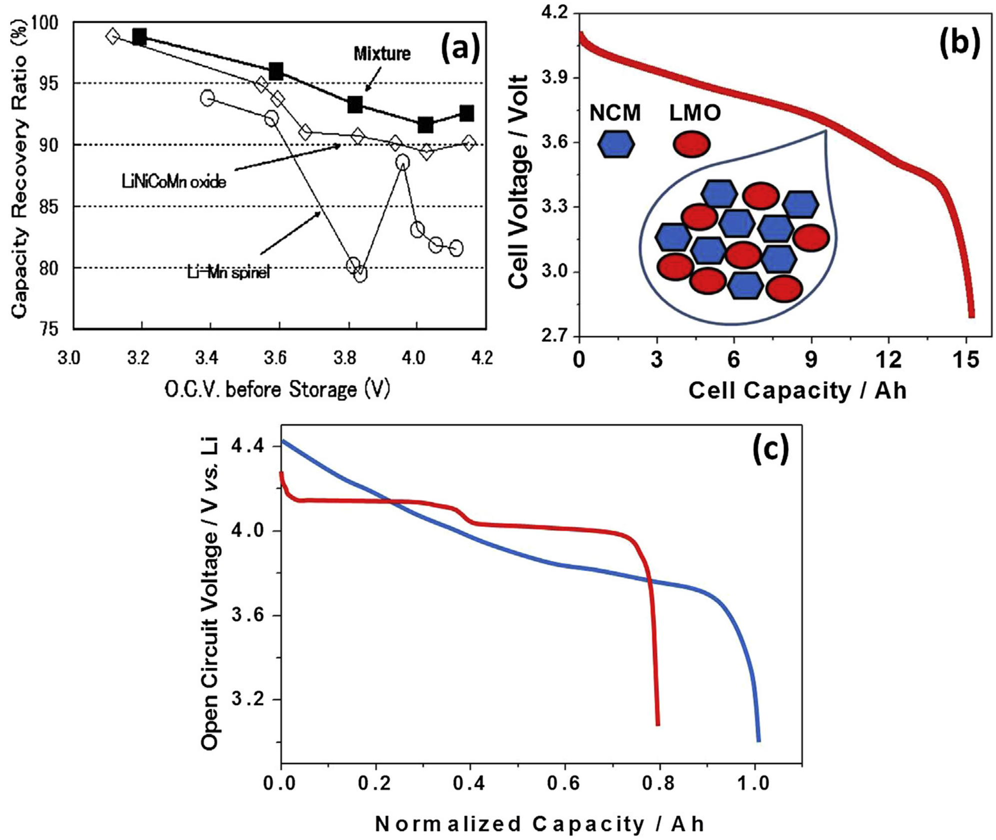

Fig. 1. (a) Capacity recovery ratio for the parent compounds spinel and NMC and their blend (40 wt% spinel) after storage for 30 days at 45 °C in 18650 cells (from Kitao et al. [1]), (b) voltage *vs.* capacity profile during 1C discharge for a commercial pouch cell made of a NCM/LMO blend and (c) open-circuit voltage *vs.* capacity (normalized) profiles for NCM and LMO in half cells [13,23].

advantages attributable to spinel may outweigh the life issues for certain applications. Although blending may be useful for optimizing performance with respect to several attributes, there may be other characteristics of the blended system that are not improved by this approach and each cathode must be carefully considered with respect to its application. Thus, blending allows the parent cathode materials to complement each other; that is, a weakness of one material alone is strengthened in the blend. The primary purpose of this communication is to survey the state-of-the-art of blended cathode materials for use in Li-ion batteries.

High-rate cycling capability to meet the power and energy requirements of hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and battery electric vehicles (BEVs) is another important characteristic for blended cathode materials to possess. In these applications, mitigation approaches such as surface treatment may be necessary to counter the loss of capacity due to shrinking and swelling of active-material particles during cycling [9,11]. Furthermore, limitations such as metal dissolution from the host metal oxide, which affects the performance of certain blended cathode materials, need to be addressed. The enhanced storage life for a cell made with a blend of $LiNi_{0.4}Mn_{0.3}Co_{0.3}O_2$ and LMO relative to a cell made with LMO alone as reported in early studies of Kitao et al. [1] is shown in Fig. 1(a). The researchers examined capacity retention during storage at 45 °C in 18650 cells and found that capacity retention was improved over spinel-only cathodes for a 40% spinel blend. To our knowledge, these results are the only example of improved cell storage life in a blended system with spinel as the parent material. In a blended cathode system, the Li insertion/extraction in one parent cathode material may be influenced by the other. Also, Li diffusion and other material characteristics influence the charge/discharge profile of the blended system. In fact, one of the major outcomes of a blended cathode system is the modification of the voltage (or state-of-charge, SOC) profile relative to that of parent cathode materials. Fig. 1(b) shows typical example of a voltage *vs.* capacity profile for a commercial pouch cell which is made with a blended cathode consisting of NMC and LMO and a graphitic anode (obtained in our laboratory). The "Ford Focus" BEV and "Chevrolet Volt" utilize pouch cell batteries fabricated using a blend of NMC and spinel. Discharge profiles for two cathodes in half cells are shown together in Fig. 1(c). The thermodynamic open circuit voltage (OCV) behavior of the blend reflects the equalized lithium activities of the individual parent compounds [2]. Several publications [1–3,6,8], account for the complex behavior associated with Li insertion/extraction dynamics in blended systems. Each parent cathode material in a blended system influences the cell SOC and Li diffusion characteristics and contributes to coulombic capacity during cycling. Due to these novel aspects, blended cathode materials are presently an active area of study. Researchers have explored parent cathode materials for blends based on layered oxides, such as $LiNi_xMn_x$-$Co_{1-2x}O_2$ (NMC) [1], NCA [2], $LiCoO_2$ (LCO) [4,7,9], $Li[Li_{0.2}Mn_{0.54}$-$Ni_{0.13}Co_{0.13}]O_2$ [3], and $xLi_2MnO_3\cdot(1-x)LiMO_2$ (M = Mn, Co, Ni)[4] [10,11], as well as spinel [5,6,8] and $LiFePO_4$ (LFP) [10]. In addition to the blended materials, which are physical mixtures, we will also discuss the Li_2MnO_3-stabilized compounds (e.g.,

[4] Also referred to as Li_2MnO_3-stabilized layered oxides or Li-rich complexes.