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Recent insights into the electrochemical behavior of blended lithium insertion cathodes: A review

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A B S T R A C T

The blending of different lithium insertion compounds has been proven to be a promising approach to design advanced electrodes for future lithium-ion batteries. Blending of certain lithium insertion compounds is done to combine the best properties of the individual active materials and to improve the energy or power density as well as cycling and storage durability. Furthermore, the blend can be tailored to meet specific requirements regarding costs, environmental issues and safety aspects. Herein, we report recent insights into the electrochemical behavior of blended lithium insertion cathodes. This review does not claim to summarize all recent literature, but rather is a critical overview of blended lithium insertion cathodes based on recent research findings. Latest thermodynamic studies enlighten certain mechanisms particularly occurring in blended insertion electrodes. Recent reports on active material combinations, including type-, mass ratio- and design-dependencies, reveal substantial improvements and synergetic effects regarding the electrochemical properties of the blended electrodes. Special experimental methods and setups are developed and applied to examine transport processes in blended insertion electrodes, revealing significant differences towards insertion electrodes containing a single type of active material. First approaches of modeling and simulation of blended insertion electrodes provide valuable information on the microscopic processes within the electrode and adequately reflect the experimental findings on the macro scale.

Contents

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1. Introduction

The public awareness of global warming and the inevitable depletion of fossil fuels have driven researchers to develop renewable energy technologies and appropriate energy storage devices. Particularly, rechargeable lithium-ion batteries (LIBs) have attracted intense attention to power hybrid (HEVs) and all-electric vehicles (EVs), owing to their long cycle and calendar life, high energy density and acceptable environmental compatibility [1–3]. Nowadays, LIBs are widely applied to power mobile electronic devices including smart devices, laptops and cameras. In contrast to such applications, LIBs for EVs require substantial improvement in terms of energy density and cost efficiency as well as enhanced safety features [4,5]. Key strategies for the successful development of advanced LIBs include the exploration of high performance positive and negative electrodes. After the commercialization of $LiCoO_2$ – graphite based LIBs by Sony in 1991, numerous alternative cathode materials, such as $LiMn_2O_4$, $LiNiO_2$, $LiFePO_4$, LiV_2O_8 and $Li_3V_2(PO_4)_3$ have been studied [6]. In spite of considerable improvements regarding energy and power density as well as cycle and calendar life, current state-of-the-art LIBs remain to be challenging for any large-scale commercialization of EVs, since their rate capability, gravimetric capacity and safety are still quite unsatisfactory.

The blending of different lithium insertion materials is a promising approach to design advanced electrodes for future LIBs. The active material of a "blended cathode" consists of a mixture of multiple lithium insertion compounds as schematically illustrated in Fig. 1. Blending of different insertion materials such as mixtures of layered-layered [7], layered-spinel [8–11], layered-olivine [12,13] and spinel-olivine [14,15] compounds is performed to combine the most favorable properties of the individual active materials and to improve the energy or power density as well as cycling and storage durability in this way.

Table 1 lists the relevant electrochemical properties of the most prominent cathode materials. The layered-type materials typically possess relatively high capacities and energy densities but show disadvantages in respect to costs, thermal stability and rate capability. The olivine-structured cathode materials exhibit improved thermal stability compared to the layered oxides but show lower electrode potentials leading to a reduced energy density. The spinel-type compounds typically exhibit higher operating voltages, lower cost, higher rate capability and better thermal stability compared to both the layered and the olivine type materials, but suffer from relatively low discharge capacity and poor cycle life performance.

Blending of different insertion materials can be used to balance these individual advantages and disadvantages in order to achieve improved overall performance as cathode material. For instance, both layered-type $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and spinel-type $LiMn_2O_4$ exhibit individual disadvantages, e.g. poor thermal stability and rate capability for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, and insufficient cycle life and poor electrochemical performance at elevated temperatures for $LiMn_2O_4$. The rate capability and the thermal stability of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ – $LiMn_2O_4$ blends is significantly improved compared to the pure $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ but still lower than that of pure $LiMn_2O_4$. On the other hand, the cycle life performance of the blend is significantly enhanced compared to pure $LiMn_2O_4$ but

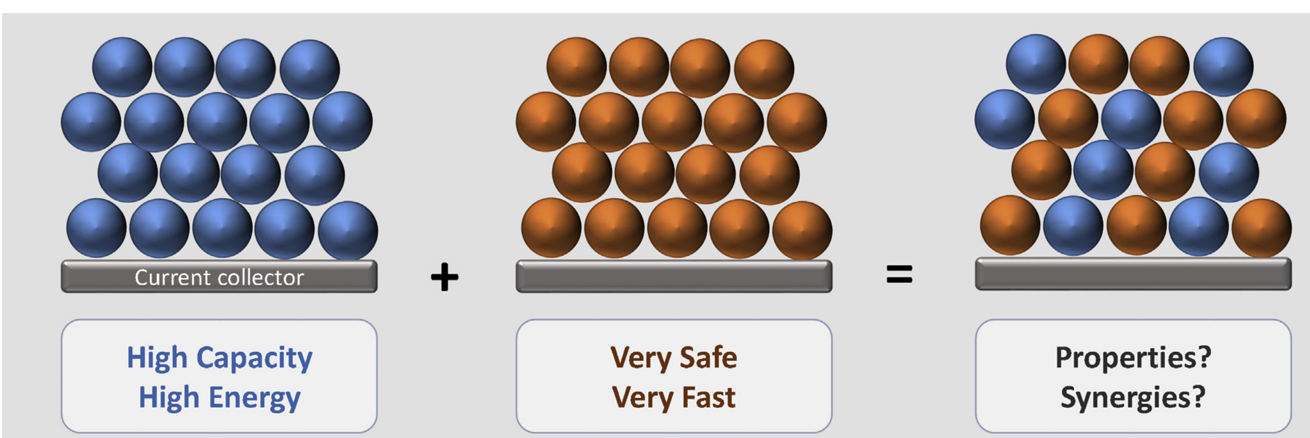

Fig. 1. Schematic illustration of the principle of blended insertion electrodes.

Table 1
Electrochemical properties of most prominent cathode materials. (The assessment of cycle life and safety properties is based on the analysis of a number of review articles concerning cathode materials for lithium ion batteries [16–20]).

Crystal structure	Compound	cutoff voltage	Avg. voltage [V]	Cycle life	Safety
Layered	$LiCoO_2$	160 (4.3) [21]	~3.9	+	–
	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	180 (4.6) [22]	~3.7	+	–
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	200 (4.4) [20]	~3.7	+	–
	$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$	183 (4.3) [23]	~3.8	+	–
	$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$	189 (4.4) [24]	~3.7	+	–
Spinel	$LiMn_2O_4$	115 (4.8) [25]	~4.1	- -	+
	$LiMn_{1.9}Al_{0.1}O_4$	100 (4.3) [15]	~4.0	–	+
Olivine	$LiFePO_4$	160 (4.0) [26]	~3.4	+ +	+ +
	$LiMnPO_4$	168 (4.5) [27]	~3.8	- -	+ +
	$LiFe_{0.3}Mn_{0.7}PO_4$	143 (4.3) [15]	~3.7	N/A	N/A
Other	$LiVOPO_4$	128 (4.5) [28]	~3.8	–	+
	$Li_3V_2(PO_4)_3$	128 (4.5) [29]	~3.6	+ +	++