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Short communication

Electrochemical performance of $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries for high-power applications

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HIGHLIGHTS

- $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries were designed and assembled for HEV application.
- The batteries exhibit high power performance and stable direct current resistance.
- Specific charge power density of 3973 W kg^{-1} was achieved at 50% depth of discharge.
- Electrochemical kinetics is performed to identify the excellent power performance.

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ABSTRACT

$LiCoO_2/SrLi_2Ti_6O_{14}$ Li-ion rechargeable batteries with ~6 Ah capacities are designed and assembled for use in hybrid electric vehicle (HEV) applications. For comparison, $LiCoO_2/Li_4Ti_5O_{12}$ batteries are also constructed using similar processing parameters. Power tests are carried out using the hybrid pulse power characterization (HPPC) method. Experimental results show that the $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries have better power performance and more stable charge/discharge direct current (DC) resistances compared with the $LiCoO_2/Li_4Ti_5O_{12}$ batteries. At a 50% depth of discharge (DOD), $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries have an excellent specific charge power density of 3973 W kg^{-1}, which can be attributed to the high Li diffusion capability and high electronic conductivity of the $SrLi_2Ti_6O_{14}$ material.

1. Introduction

Safety and cycling life are important concerns for high-capacity Li-ion batteries used in electric vehicles and energy storage applications. Thus, the spinel $Li_4Ti_5O_{12}$ has gained significant attention because of its improved safety and cycling properties over carbon-based anodes. These advantages include the zero-strain characterization during Li-ion intercalation/de-intercalation, higher operation potential (above the potential of the solid electrolyte interface (SEI) layer formation), and safer overcharging behavior [1–7].

However, the lower operating voltage of lithium-ion batteries using $Li_4Ti_5O_{12}$ as the anode leads to a large decrease in energy density for Li-ion batteries, as well as shorter endurance mileage compared to carbon-based anodes when used in electric vehicles [8]. In addition, when producing Li-ion batteries it is difficult to increase the volume energy density by increasing the coating content of the active material on the current collector. This difficulty is caused by the large specific surface area and lower tap density of $Li_4Ti_5O_{12}$.

$SrLi_2Ti_6O_{14}$, which has a theoretical capacity of 262 mAh g^{-1} [9], possesses a three-dimensional structure with the *Cmca* space group in which Li ions can migrate quickly because of the structure's high diffusion coefficient, allowing for excellent high-drain performance. Belharouak et al. reported that an $SrLi_2Ti_6O_{14}$ electrode had lower area specific impedance (ASI) than a $Li_4Ti_5O_{12}$ electrode [10]. Dambournet et al. reported measuring a 92 mAh g^{-1} capacity for an $SrLi_2Ti_6O_{14}$ electrode at an approximate rate of 8C; this capacity was about 83.6% of its 1C capacity, exhibiting excellent rate performance [9]. Thus, $SrLi_2Ti_6O_{14}$ was considered to be a potential replacement for $Li_4Ti_5O_{12}$ because of its lower operating voltage (~1.40 V vs. Li^+/Li), lower ASI, and higher tap density, allowing for

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the possibility of a higher energy density while maintaining good power performance [11]. To our knowledge, there have been no reports using $SrLi_2Ti_6O_{14}$ as an anode in Li-ion batteries designed for hybrid electric vehicle applications.

In this work, batteries for HEV applications with ~6 Ah capacities were designed and assembled using either $SrLi_2Ti_6O_{14}$ or $Li_4Ti_5O_{12}$ as the anode. The electrochemical performance of the two kinds of batteries was investigated, focusing on the power performance; the differences in those results are discussed in this paper.

2. Experimental

2.1. Battery assembly and power performance test

Li-ion batteries with 6 Ah capacities designed for HEV applications were constructed using $LiCoO_2$ as the cathode and $SrLi_2Ti_6O_{14}$ (provided by MGL Co. Ltd., China) as the anode. The proportion of active material in the anode electrode was a 92% mass fraction. The $SrLi_2Ti_6O_{14}$ coating content on the current collector was about 210 g m^{-2}. The electrolyte was 1 mol L^{-1} $LiPF_6$ in ethylene carbonate/dimethyl carbonate/ethyl–methyl carbonate mixtures (1:1:1, V/V), and the separator was UPZS40 (UBE, Japan). A lamination-type battery was constructed, as shown in Fig. 1. The assembled batteries were somewhat cathode limited (3% capacity excess of the anode relative to cathode). For comparison, $Li_4Ti_5O_{12}$ was purchased from a vender (BTR Co. Ltd., China) and used as the anode material to assemble $LiCoO_2/Li_4Ti_5O_{12}$ full cells with the same anode electrode formula, electrolyte, membrane, and cathode as the $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries. The actual reversible specific capacities (vs. Li^+/Li in half-cell) of the $LiCoO_2$, $Li_4Ti_5O_{12}$ and $SrLi_2Ti_6O_{14}$ in this work are 164 mAh g^{-1}, 172 mAh g^{-1} and 124.3 mAh g^{-1}, respectively. Because the stable reversible capacity of $SrLi_2Ti_6O_{14}$ is about two-thirds that of $Li_4Ti_5O_{12}$ [9], the specific coating content of the $SrLi_2Ti_6O_{14}$ electrode on the current collector was approximately 1.5 times that of the $Li_4Ti_5O_{12}$ electrode. After a roll-pressing process, the final electrode thickness of $SrLi_2Ti_6O_{14}$ and $Li_4Ti_5O_{12}$ are 95 μm and 73 μm, respectively. The other processing parameters were similar for the two anode materials.

The batteries were first charged to 3.2 V for the $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries and 2.8 V for the $LiCoO_2/Li_4Ti_5O_{12}$ batteries at a 0.1C rate, and were then discharged to 1.5 V at a 0.1C rate at 25 °C. After degassing and a final sealing operation, the batteries were charged and discharged three times at a 1.0C rate at room temperature for the following power test.

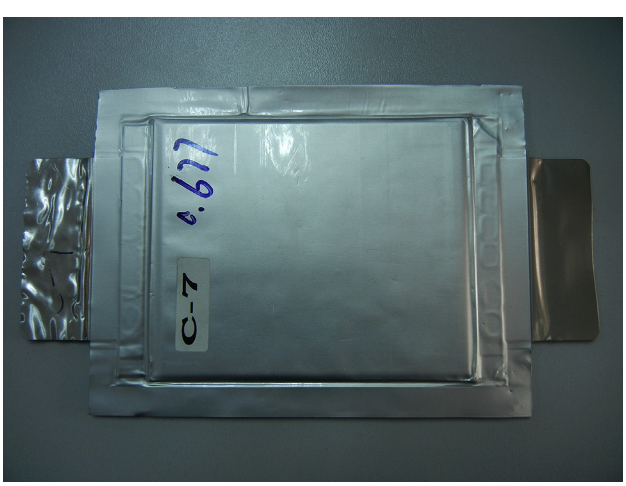

Fig. 1. Experimental pouch battery with 6 Ah capacities, designed for power applications.

Power comparison tests were performed on the batteries at room temperature according to the hybrid pulse power characterization (HPPC) method [12]. The power test was carried out using high-power charge–discharge equipment (BT2000, 5V-300A, Arbin, USA).

2.2. Electrochemical characterization of materials

The electronic conductivity of the $SrLi_2Ti_6O_{14}$ and $Li_4Ti_5O_{12}$ powders were carried out on a conductivity meter (Shanghai SB118, China) using a conventional four-point probe method at room temperature. The specific surface areas of the two powders were measured on a Gemini2360 instrument (Micromeritics, USA) using an N_2 adsorption-desorption process at 77 K. The tap density of each material was examined using a tapping apparatus (FZS4-4B, IRsID, China). X-ray diffraction patterns of powders were collected on a Bruker D8 ADVANCE Powder Diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) between 10 and 90° (40 kV, 40 mA, step size = 0.02° and a count time = 0.2 s/step.). Molar volume data of powders were deduced from Rietveld refinements, which were performed using Bruker Topas4.2 software.

Electrodes used for half-cells, were made by casting a slurry of 90 wt.% active material oxide, 5 wt.% conductive reagent (Timcal, super-P), and 5 wt.% PVDF binder (Kynar, ARKEMA) in a *N*-methyl-2-pyrollidinone (NMP) solvent onto a Cu-foil substrate. The slurry was cast using a doctor blade. The cast laminates were dried in air at 120 °C for 2 h and then in a vacuum at 70 °C for 8 h. The electrodes were then pressed to fixed thicknesses of 35–40 μm. Lithium coin cells (CR2032) were fabricated in an Ar-filled glove box (<1 ppm O_2, MBraun, Germany). Lithium metal was used as the counter electrode, a Celgard 2400 microporous polypropylene membrane as the separator, and 1 M $LiPF_6$ in a 1:1:1 volume fraction of ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl-methyl carbonate (EMC) as the electrolyte. Charge–discharge formation and galvanostatic intermittent titration technique (GITT) experiments were performed on a multichannel potentiostatic–galvanostatic system (CT2010A, Land, China). For the GITT measurement, the coin cells were charged and discharged with a constant current flux for a given time followed by an open-circuit stand for a specified time interval.

3. Results and discussion

3.1. Electrochemical performance of full cells

Fig. 2 shows the charge–discharge curves for the full cells, which were designed for HEV applications; each used $SrLi_2Ti_6O_{14}$ or $Li_4Ti_5O_{12}$ as its anode. The basic parameters of the batteries are listed in Table 1. Fig. 2 shows that the $LiCoO_2/SrLi_2Ti_6O_{14}$ battery curves have a higher voltage plateau than the $LiCoO_2/Li_4Ti_5O_{12}$ batteries, resulting in greater energy storage at the same capacity. Because of the lower reversible capacity of $SrLi_2Ti_6O_{14}$ compared with $Li_4Ti_5O_{12}$, more active material ($SrLi_2Ti_6O_{14}$) was used in the $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries for designs of the same capacity as $LiCoO_2/Li_4Ti_5O_{12}$ batteries. This addition causes the $LiCoO_2/SrLi_2Ti_6O_{14}$ battery to weigh more than the $LiCoO_2/Li_4Ti_5O_{12}$ battery. However, because of the higher operating voltage of the $LiCoO_2/SrLi_2Ti_6O_{14}$ batteries, as shown in Fig. 2 and Table 1, they had higher energy densities than the $LiCoO_2/Li_4Ti_5O_{12}$ batteries.

Fig. 3 shows the rate curves for the two kinds of batteries. Their 25C rate discharge capacity ratios are close to each other. In contrast, the charge capacity ratios of the two kinds of batteries are very different; at a 15C rate they have 88.3% and 63.6% of the 1.0C capacity for the $LiCoO_2/SrLi_2Ti_6O_{14}$ and $LiCoO_2/Li_4Ti_5O_{12}$ batteries, respectively. The fast-charge performance of the $LiCoO_2/SrLi_2Ti_6O_{14}$