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Cathodes with intrinsic redox overcharge protection: A new strategy towards safer Li-ion batteries

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HIGHLIGHTS

- A novel safety strategy to avoid overcharging, i.e. solid-state anti-overcharge additive, is proposed.
- The strategy can provide a high-potential and a long-period of anti-overcharge performance.
- The effectiveness of the solid-state anti-overcharge additives is confirmed in $LiCoO_2$/C and $LiMn_2O_4$/C full cells.

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ABSTRACT

Overcharge safety is the most crucial problem facing especially large-sized lithium-ion batteries (LIBs) packs owing to the inevitable inhomogeneity of charge-state for each cell. We propose a fresh safety strategy to avoid overcharging, i.e. the use of a solid-state anti-overcharge additive to perform an intrinsic overcharge protection. The mechanism is triggered from a solid-state composite cathode obtained by typically mixing a pre-selected transition-metal oxide with a certain cathodes thus constituting a composite cathode. The effectiveness of this strategy is demonstrated with an example of $LiCoO_2$/CuO (95:5 by weight) composite, which exhibits high-potential (up to 5 V vs. Li^+/Li) and long-period (month-level) anti-overcharge performance. It is found that the additive does not hurt the electrochemical cycling performance under normal operational conditions. This novel safety strategy is simple and flexible, which may open a new window to develop safer LIBs systems.

1. Introduction

For large-scale applications of lithium-ion batteries (LIBs) in the situations like solar or wind energy plants or grid storage, safety will become major criterion for the general acceptance of this electrochemical technology [1–6]. Overcharge is the most popular and dangerous problem because it occurs particularly in large-sized LIBs systems with multiple cells owing to the inevitable inhomogeneity of charge-state of individual component cells [7–11]. In the galvanostatic mode, overcharge leads to unwanted high-voltages in which truly serious consequences root, including thermal runaway [8], gas generation [9], short-circuits [10] and ultimately fire or explosion [11]. Therefore, the control of voltage-runaway is key to overcome overcharge hazards. As an external protection, electronic-circuit is commonly used but not inherently reliable owing to occasional function-failure thus leading to more serious hazards [7]. Hence, an intrinsic mechanism should be developed to achieve more reliable overcharge protection. The currently established solution is to use liquid electrolyte additives, which function through reversible oxidation/reduction starting at a defined voltage slightly higher than the end-of-charge voltage to consume excess charge [7,12–15]. However, such additives suited for higher-voltage cathode materials (e.g. $LiNi_{0.5}Mn_{1.5}O_4$ (4.7 V) [16], $xLi_2MnO_3\cdot(1-x)LiMO_2$ (above 4.6 V) [17]) are very rare, and

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subject to numerous severe limitations, including cost, electrochemical and chemical stability, compatibility with the battery components, and especially definite solubility requirement. These shortcomings significantly restrict the feasibility of this development.

Herein, we propose and confirm a novel safety strategy to avoid overcharging, i.e. solid-state anti-overcharge additives, an intrinsic overcharge protection mechanism triggered from solid-state composite cathodes. These composite cathodes provide an appropriately high triggering-potential (up to 5 V vs. Li^+/Li) and a long-period (month-level) of anti-overcharge performance. To our best knowledge, this is the first time that such a concept of cathodes providing intrinsic overcharge protection with a good performance has been reported. In this study, the $LiCoO_2/CuO$ composite is used as an example to demonstrate the fundamental mechanism.

2. Experimental

2.1. Materials and chemicals

$LiCoO_2$ (Huatian Co., Ltd, China), $LiMn_2O_4$ (Jinhe Co., Ltd, China) and CuO (Sinopharm Co., Ltd, China) were used as raw materials. To obtain the $LiCoO_2/CuO$ composite materials, the suspension containing dispersed $LiCoO_2$ and CuO powder in alcohol was fully stirred and dried to evaporate solvent. For $LiCoO_2/CuO$ materials, there were four samples of different CuO contents: 0%, 5%, 30% and 100% (pure CuO). In addition, $LiMn_2O_4/CuO$ (5%CuO) samples were obtained through the same solution mixing method. The above composite materials were all used as cathode (positive) materials. The cathode electrode laminates were formed by casting a mixture of $LiCoO_2/CuO$ (or $LiMn_2O_4/CuO$), acetylene black and poly(-vinylindene fluoride) (PVDF) (mass ratio of 84:8:8) onto Al foil. They were dried and then punched into 14 mm diameter discs. The electrode active-substance loading was 12–15 mg (around 9.8 mg cm^{-2}) for each electrode disc. Lithium foil or graphite electrode was used as the anode (negative) electrode. The graphite electrode was formed by casting a mixture of graphite and PVDF (mass ratio of 92:8) onto Cu foil then punched it into 14 mm diameter discs. Battery-grade electrolyte (Guotai-Huarong, 1M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by mass)) and polypropylene separator film (Celgard) were used as received.

2.2. Batteries fabrication and characterization

Two kinds of cells were assembled in an argon-filled glove box (MBraun Labmaster 130) with 1 ppm H_2O and 1 ppm O_2 content. Electrochemical performance tests were carried out using CR2032 coin-type cells. The amount of electrolyte in each coin-type cell is generally around 0.09 mL unless otherwise noted. To monitor the gas generation, pressure measurements were performed using a pressure-container cell setup (MTI Inc., Hefei) equipped with a pressure gauge. In each pressure-container cell, the same cathode and anode discs as coin cells were used, but the amount of electrolyte is required at around 3 mL. The phase compositions and crystal structures were characterized by X-ray diffraction (XRD) (Rigaku TTR-III, Cu Kα radiation). Surface elemental composition analyses were determined by energy-dispersive X-ray spectroscopy (EDS) based on scanning electron microscopy (SEM, JEOL-6390 LA). The content of Cu element in electrolyte was detected using inductive coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, Perkin Elmer Corporation, USA). Electrochemical measurements were performed using a Battery Testing System (BTS-3008W, Neware, Shenzhen). The internal DC resistance was measured with current interruption technique. A resistance is determined based on a measurement of $\Delta V/\Delta I$ between a base current and a high current step. This was carried out by cutting off the current (zero current) for 1 min before charging process in each cycle, and collecting the changes of voltage (ΔV) and current (ΔI) before and after this interruption. Thus, the DC resistance are calculated as $R_{dc} = \Delta V/\Delta I$. All cells were overcharged with constant current (CC) mode.

3. Results and discussion

3.1. Effect of voltage-control on $LiCoO_2/CuO$ composite cathode

The characteristic features leading to this study are revealed from the first charge voltage profile of a bare CuO(Al foil)/Li cell (Fig. 1a), exhibiting a short 5 V interval, followed by a drastic voltage-drop and a long-time low-voltage plateau. For such a voltage curve, Cu^{2+} ions are released into the electrolyte and then reduced into Cu^+ to establish an important durable Cu^{2+}/Cu^+ redox shuttle, which will be detailed later. As controlling voltage-runaway is key in the context of overcharge protection, such a behavior is exciting. Indeed, the usefulness of CuO as an additive is confirmed by the overcharge voltage profile of a ($LiCoO_2$ + 5%CuO)/Li cell, revealing similar features including voltage-drop and long-time low-voltage plateau (Fig. 1b). For comparison, an overcharged $LiCoO_2$/Li cell initially displays an identical profile before it

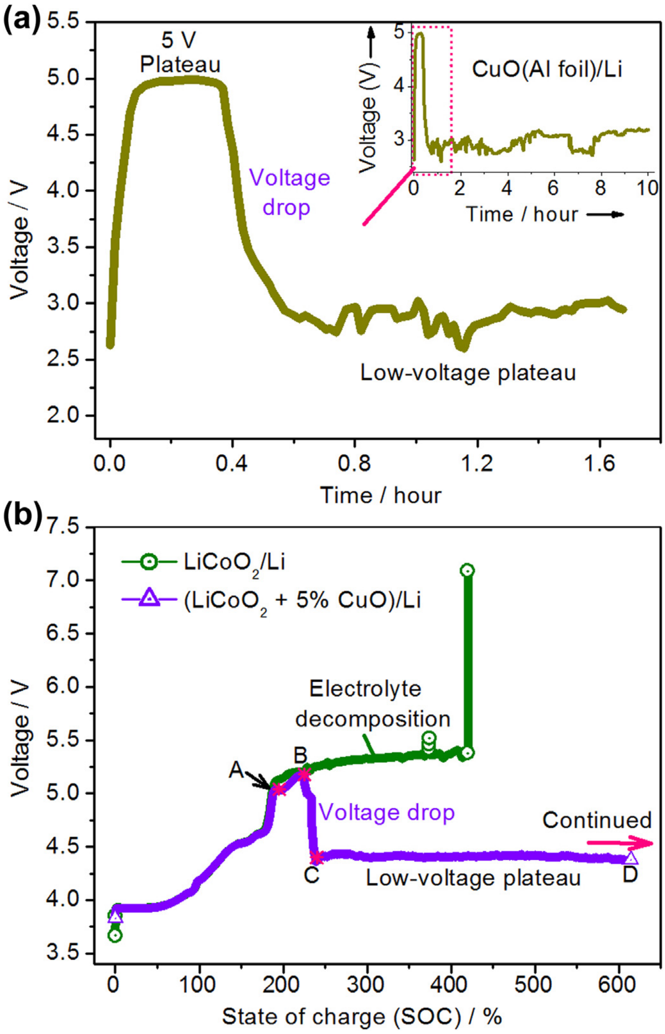

Fig. 1. Overcharge voltage profiles: a) CuO(Al foil)/Li coin cell (0.3 mA current). b) $LiCoO_2$/Li and ($LiCoO_2$ + 5%CuO)/Li coin cell (C/8 rate).