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Electrochemical and safety performance of Li pre-doping free cell using tin-phosphate glass-silicon composite anode

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HIGHLIGHTS

- A Li pre-doping free cell using the $SnO-P_2O_5$ glass-Si composite anode was developed.
- A discharge capacity of 187 mAh g^{-1} as the cathode capacity was observed.
- The long cycle performance of over 100 cycles was achieved.
- The cell displayed an excellent performance (−20–60 °C) and a good rate performance.
- No thermal runaway was observed during the nail penetration test.

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ABSTRACT

The Li pre-doping free cells using tin-phosphate glass (GSPO)-silicon composite anodes and lithium-rich layered oxide (LR-NMC) cathode were developed, in which the irreversible capacity of the cathode was utilized in order to compensate that of the anode. The irreversible capacity was equalized to that of the cathode at a Si/(GSPO + Si) mass ratio, *r*, of 0.8. The cell using the composite anode of $r = 0.8$ displayed a discharge capacity of 187 mAh g^{-1} as the cathode capacity at 30 °C and the 0.1C-rate. The long cycle performance of over 100 charge–discharge cycles was achieved. The cells also showed an excellent high- and low-temperature performance and a good rate performance. A stable performance was observed for over 50 cycles at 60 °C and the 0.5C-rate, and a high capacity of ca. 100 mAh g^{-1} as the cathode capacity even at −20 °C and the 0.2C-rate. The cell could discharge even at the 10C-rate. Furthermore, the Li pre-doping free cell showed an outstanding safety performance during the nail penetration test. When the 1500 mAh cell using the composite anode was penetrated by a nail, no thermal runaway was observed during the test.

1. Introduction

Lithium-ion batteries (LIBs) are attracting much attention as the power source for hybrid electric vehicles (HEVs), electric vehicles (EVs) and stationary energy storage systems. Batteries for these applications require a significant high specific energy capacity and power density. Significant efforts have been made to improving their energy density and power density. Regarding the anode material, alloy-based anode materials, such as tin [1–3] and silicon [4–6], have been considered as the next-generation anode materials due to their specific capacities higher than that of conventional graphite [1].

Our group recently developed a tin-phosphate glass (glassy $SnO-P_2O_5$, GSPO) anode material prepared via a melt quenching process [7,8]. The GSPO anode has a stable cycle life with a high reproducible capacity of more than 550 mAh g^{-1}. It is believed that the glass structure of GSPO, in which the tin nanocrystals are surrounded by a lithium phosphate glass matrix, was considered to be responsible for suppression of the volume change during the charge–discharge process, resulting in an outstanding cycle

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performance. The GSPO anode is also useful over a wide operating temperature range. The full-cell consisting of the GSPO anode and glass-ceramic $LiFePO_4$ (GC-LFP) [9] cathode displayed an excellent low-temperature and high-temperature performance in which the stable cycle-performance with a capacity of 110 mAh g^{-1} at the 0.2C-rate and −20 °C and a capacity of 140 mAh g^{-1} at the 10C-rate and 60 °C were achieved. Furthermore, the GSPO anode provides an outstanding safety performance during the nail penetration test. The 660 mAh laminated-type pouch cell using the GSPO anode and GC-LFP cathode showed a slight decreasing cell voltage and slightly increasing nail internal temperature to 49 °C and cell surface temperature to 29 °C during the nail penetration test, in which the tin nanocrystals surrounded by the glass matrix in the GSPO is the key factor for its safety and the GSPO anode locally discharged in the internal short-circuit part due to the insulating nature of the GSPO.

As already mentioned, the authors believe that the GSPO can be a good candidate for the next-generation anode providing an excellent electrochemical performance over a wide temperature range along with a safe performance. However, the GSPO anode has a significant irreversible capacity of ca. 54% for the 1st charge–discharge (cut-off voltage: 0–1.0 V) [7]. Therefore, the Li pre-doping process or pre-lithiation process of the anode is required to eliminate the irreversible capacity of the anode prior to assembling the full-cell, thus avoiding a decrease in the cell capacity by an electrochemical method using lithium metal as the counter electrode [10,11] or directly contacting the lithium metal foil [12,13] or stabilized lithium metal powder [14] on the anode surface. Although these methods are useful for the elimination of the irreversible capacity of the anode, such processes are undesirable from the view point of cost and safety, especially in industries, and pose obstacles to the practical use of the GSPO anode for the LIBs. Therefore, it is essential to develop a technique without the need of a Li pre-doping process in order to fully utilize the GSPO.

With respect to the cathode material, the cathode should have a higher capacity than the currently use lithium cobalt oxide ($LiCoO_2$, LCO) or lithium nickel manganese cobalt oxide ($LiNiCoMnO_2$, NMC), which provides a specific energy capacity of ca.150 mAh g^{-1} and ca.170 mAh g^{-1}, respectively. In recent years, a lithium-rich layered oxide (xLi_2MnO_3–$(1-x)LiMO_2$ (M = Mn, Ni, Co, etc.), LR-NMC) is considered to be a promising cathode material to substitute for the conventional cathode material [15–18]. Although the LR-NMC cathode exhibits much higher capacities above 200 mAh g^{-1} over 4.5 V [17,18], the LR-NMC has a relatively high irreversible capacity during the 1st charge–discharge due to Li_2O removal from the structure [19]. The high irreversible capacity is a problem for the design of full cells, resulting in a lower energy density of the cells, similar to the GSPO.

The authors then focused on the high irreversible capacity of the LR-NMC cathode material in order to supply the lithium to be consumed at the anode. In this system, the pre-doping of lithium to the anode is not required. However, the irreversible capacity of the GSPO anode is too high to be compensated by the LR-NMC. Therefore, in the present study, the irreversible capacity of the anode was adjusted by preparing a composite anode with the GSPO and Si, which has a high reversible capacity and low irreversible capacity, to be sufficiently eliminated by that of the LR-NMC cathode. However, it was expected that the degradation of the cycle performance of the cell might be caused by the addition of Si to the anode because of the significant crystallographic volume changes in the Si during the charge–discharge process.

This study then attempted to develop Li pre-doping free cells using the GSPO-Si composite anodes and LR-NMC cathode, which does not require the Li pre-doping process and provides a high energy density, and evaluated the electrical performance of the cells. Furthermore, the safety performance of the 1-Ah-class, Li pre-doping free cell was also investigated using the nail penetration test.

2. Experimental

2.1. Preparation of the electrodes and cells

For the preparation of the GSPO-Si composite anodes, a slurry of mass composition, GSPO-Si: ketjen black (KB): polyimide (PI) = 80: 2: 18, was prepared by the following procedure. The GSPO powder, synthesized via a glass melting process as previously described [7], was blended with Si powder (Silgrain, e-Si-400, Elkem) in order to adjust the irreversible capacity of the anode at various Si/(GSPO + Si) mass ratios, $r = 0$ (GSPO), 0.2, 0.5, 0.8, and 1 (Si). These powders, KB (ECP-300JD, Lion) and PI resin (Toray industries) as the binder were mixed to form a slurry. The slurry was spread onto 10-μm thick stainless steel (SUS) foil (NSSC 190, Nippon Steel & Sumikin Materials), followed by a heat treatment for curing at 360 °C for 1.5 h under an argon atmosphere.

For the preparation of the LR-NMC cathodes, a slurry of mass composition, LR-NMC: acetylene black (AB, Denka Black, Denki Kagaku Kogyo): polyvinylidene fluoride (PVDF, #1120, Kureha Battery Materials Japan) = 90: 5: 5, was prepared by the following procedure. The LR-NMC supplied by Nihon Kagaku Sangyo was mixed with AB and PVDF as the binder to form a slurry. The slurry was spread onto aluminum foil, then pressed between a pair of metal rollers.

CR2032-type coin cells along with half-cells and full-cells were fabricated. For the half-cells, Li foil was used as the counter electrodes. The full-cells were fabricated using the GSPO-Si composite anodes and LR-LMC cathodes in which the charge capacities (mAh) in the 1st cycle of the anodes and cathodes were equalized to obtain the maximum energy density for the reasons to be discussed later. A pouch cell was prepared for the measurement of the cathode and anode voltages versus the reference potential, in which Li foil was used as the reference electrode. The 1-Ah-class, laminated-type pouch cells consisting of the GSPO-Si composite anodes and LR-NMC cathodes were also fabricated.

1 mol dm^{-3} $LiPF_6$ in EC/DEC (1/1, v/v), EC/GBL (1/1, v/v) or PC was used as the electrolyte solution. A glass filter and SiO_2 coated polyolefin non-woven fabric (Japan Vilene) as the separator were used in the coin cells and laminated-type pouch cells, respectively.

2.2. Electrochemical measurement

The cell performance was evaluated using a charge–discharge apparatus (BLS series, Keisokuki Center) at various charge–discharge rates between −20 °C to 60 °C. For the GSPO-Si composite half-cells, the voltage range was 0.001–1.0 V vs. Li/Li^+. For the LR-NMC half cells, the 1st charge was carried out to 4.6 V vs. Li/Li^+ to activate the LR-NMC cathode, then the subsequent charge–discharge was carried out in the voltage range of 2.0–4.3 V. For the full-cells consisting of the GSPO-Si composite anode and LR-NMC cathode, the 1st charge and discharge were carried out to 4.6 V and 1.5 V, respectively, then the following charge–discharge was carried out in the voltage range of 2.0–4.2 V.

2.3. Safety evaluation

The safety evaluation of the 1-Ah-class, laminated-type pouch cell based on the nail penetration test using a safety evaluation apparatus (Toyo system) was performed. The fully-charged cells were used for the test. The fully-charged cell was penetrated by an iron wire nail (JIS-N65; 65-mm length and 3-mm diameter) at the