

Advanced sodium-ion rechargeable battery based on a Sn/C anode and layered oxide framework cathode

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Introduction

Lithium batteries are the power sources of choice for popular mobile electronics and accordingly, they are fabricated at a yearly rate of several billions [1] units; in addition, there are concrete possibilities that these batteries can also aggressively enter in the electro mobility and renewable energy source markets.[2] These high expectations of market expansion have started to rise some concern on the long range availability of lithium. Although globally abundant, lithium resources are concentrated in large quantity in few countries in South America [3] and this may induce the risk of market dependence. Therefore, there is an increasing interest in non-lithium, cost-effective energy storage systems. Among them, sodium batteries, due the almost infinite resource of the metal, are the most appealing as immediate alternatives to lithium batteries.

A series of recently reported relevant results [4] has triggered an increasing industrial and academic interest in room temperature sodium-ion batteries able to effectively compete with the lithium ion counterparts in terms of cycle life, rate capability and energy density. A very important contribution in this direction has been provided by Komaba and co-workers with the development of rechargeable batteries based on the electrochemical combination of hard carbon anode and an oxide framework $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode. This important result has demonstrated the feasibility of the sodium-ion concept and hence, opened the route for further studies in the field. Following this trend, we report here a new type of sodium-ion rechargeable battery obtained by combining a nanocomposite tin-carbon, Sn-C anode with an optimized $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode

Experimental

$\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ powders were prepared via a co-precipitation process. First, stoichiometric amounts of high-purity $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ were uniformly mixed and dissolved in distilled water up to a concentration of 2.0 mol dm^{-3} . This metal solution was pumped into a continuously stirred tank reactor (CSTR, 4 L) under N_2 atmosphere. At the same time, a NaOH solution of 2 mol dm^{-3} and an appropriate amount of NH_4OH solution as a chelating agent were also separately pumped into the reactor by carefully controlling pH, temperature, and stirring speed of the mixture. After completion of the reaction, the precipitated particles were filtered, washed, and dried at $110 \text{ }^\circ\text{C}$ to remove absorbed water. The obtained hydroxide precursors were thoroughly mixed with Na_2CO_3 (molar ratio of Na/transition metals = 1.02) and calcined at $820 \text{ }^\circ\text{C}$ for 48

h in air with a heating rate of $3 \text{ }^\circ\text{C min}^{-1}$ and then quenched under room temperature.

The crystalline phase of the synthesized materials was characterized by powder x-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu-K α radiation and the related patterns were analyzed The FULLPROF Rietveld program.¹⁷ The morphology of the precursor and the as-synthesized powders were observed by scanning electron microscopy (SEM, JSM 6400, JEOL Ltd., Japan). The chemical compositions of the prepared powder were analyzed with atomic absorption spectroscopy (AAS, Vario 6, Analytik Jena, Germany).

The electrochemical tests were performed in a CR2032 type coin-type cell adopting Na metal (Alfa Aesar., USA) as the anode. The cathodes were fabricated by blending the prepared $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ powders (85 wt%), carbon black (7.5 wt%), and polyvinylidene fluoride (7.5 wt%) in *N*-methylpyrrolidinone. The slurry was then cast on an aluminum foil, dried at $110 \text{ }^\circ\text{C}$ for 12 h in a vacuum oven, and punched out to form electrode disks. The electrolyte was a 1.0 M solution of NaClO_4 in a 98:2 volumetric mixture of propylene carbonate and fluoroethylene carbonate (PANAX ETEC Co., Ltd., Korea), PC-FEC. All cells were prepared in an Ar-filled dry box and cycled in a constant current mode at a 0.1 C rate ($1\text{C} = 120 \text{ mAh g}^{-1}$) within two voltage ranges. i.e. 2.2-4.0 and 2.2-4.2 V versus Na

Results and discussion

Figure 1 show the Rietveld refinement of the XRD data for the as-synthesized $\text{Na}_{1.00}(\text{Ni}_{0.49}\text{Mn}_{0.51})\text{O}_2$ powders annealed at $820 \text{ }^\circ\text{C}$ in air, carried out assuming a space group of R-3m belonging to a rhombohedral structure. The observed pattern is consistent with the simulated one. A typical feature here is that the diffraction intensity of the (003) peak is lower than that of the (104) peak. To be noticed that in the corresponding Ni-based lithiated transition metal oxides with a rhombohedral structure, the (003)/(104) peak ratio is assumed as to be a measure of cation mixing in the Li layer. Therefore, it is expected that the same rule applies for the sodium compounds as well.

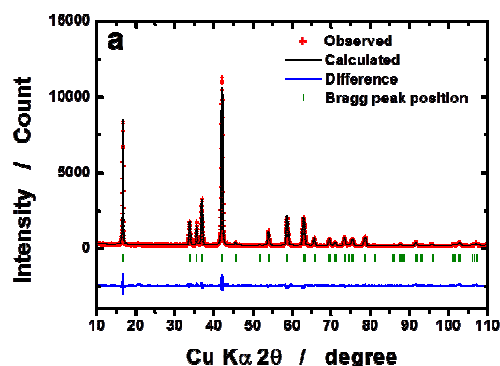


Fig. 1 Rietveld refinement of XRD patterns of $\text{Na}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ powders.

References

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