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Co_3O_4 negative electrode material for rechargeable sodium ion batteries: An investigation of conversion reaction mechanism and morphology-performances correlations

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HIGHLIGHTS

- The reversible electrochemical reaction mechanism involves CoO instead of Co_3O_4.
- Electrode presodiation decreases noticeably the first cycle capacity loss.
- Presodiated electrode shows a capacity of 600 mAh g^{-1} after 50 cycles.

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ABSTRACT

Transition metal oxides have recently aroused a renewed and increasing interest as conversion anode materials for sodium ion batteries. Being their electrochemical performances strongly dependent on morphological aspects, has been here proposed a straightforward approach to modulate morphological characteristics of a transition metal oxide (Co_3O_4) using a low cost synthetic route. The as obtained optimized morphology allows the realization of high practical specific capacities, higher than 500 mAh g^{-1} after 50 cycles, and represents a valid candidate for further optimization. In addition to the morphology-performance correlations, the reaction mechanism beyond the electrochemical behavior was also investigated revealing the role of the CoO phase in the charge/discharge process. Finally, an electrode pre-sodiation treatment for conversion materials is presented: it has been indeed demonstrated that it sensibly decreases the irreversible capacity correlated to the first cycle and improves cycle ability.

1. Introduction

Lithium-ion battery (LIB) technology has ended to cover, in almost 25 years, the 95% of the secondary battery market for cordless device (mobile phones, laptops, cameras, working tools) [1] thanks to its versatility, high round trip efficiency and adequate energy density. Its market permeability also relates to automotive field, where a high energy density is desirable over a high power density. The recent introduction of LIBs to cars propulsion (Hybrid electric vehicles HEV, Plug-in hybrid electric vehicle PHEV, and Electric vehicles EV) is expected to lead in a few years to a dramatic increase in LIBs technology exploitation. This aspect, together with political issues related to in-homogeneity distribution of raw materials for LIB manufacturing, concurred to arise a growing concern in relation to the future sustainability of this technology [2–4]. The sodium-ion battery (SIB) system seems to be a valid and more sustainable alternative to Lithium economy, according to the easier procurement of raw materials and the rather similar chemistry between Li and Na [5,6]. SIBs would be a better choice, especially for large scale application, such as stationary storage connected to renewable power sources, in which costs are critical [7]. Developing efficient SIBs worthwhile to be employed in on-grid storage and other fields may lower the exploitation load over LIBs technology,

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reducing the strategic interest for the raw materials.

Many efforts have already been made in the design and characterization of both anode and cathode materials for Na-ion batteries so far [8,9]. For what concern cathode side of SIBs, promising results have been achieved in relation to the stability and charge retention of electroactive intercalation materials as widely described in the review by Masquelier et al. [10].

In this extensive dissertation the authors go through several promising polyanionic ($(PO_4)^{2-}$, $(SiO_4)^{4-}$ and $(SO_4)^{2-}$) based compounds proposed in recent years as cathode materials in LIBs, in the place of fully investigated transition metal oxides ($Li_{1-x}MO_2$ with M = Co,Ni,Fe,Mn). The performances of the latter in a Na environment are also collected. As a result, polyanion frameworks are capable of an efficiently sodium cations intercalation, with a high structure retention through cycling. The advantages in their utilization resides also in the polyanion inductive effect that boosts the cathode operating voltage, higher stability, large variety of obtainable structure and atoms arrangements and the lower costs of manufacturing. Anode materials, conversely, still represent a challenging topic needy to be investigated. Many solutions have been proposed to overcome the intrinsic limits of negative electrode materials, namely the low practical specific charge and the fast degradation of electrode characteristics. Other delicate features that have to be taken into consideration are the operating voltage, that must be suitable for the utilization of the investigated compound as an anode inside the cell and the problematic irreversible capacity related to the first cycle. For these reasons several classes of materials have been taken into account [6,11]. Transposition of graphitic anodes already employed in LIBs to sodium environment has been considered at first glance: nevertheless, since intercalation of the larger sodium ion into graphite sheets structure induces exfoliation, nano-structured hard-carbons have been investigated instead [12–14]. The performances are controversial and are affected by high irreversible capacity during the first charge/discharge loop and sloping charge/discharge profiles. Sodium alloying with 14th and 15th group elements (Sb [15,16], Sn [17], Ge and In [18]) has been also exploited to obtain anode materials for SIBs: the high theoretical capacity of sodium rich phase Na-Sn alloy (847 mAh g^{-1} for $Na_{15}Sn_4$) led to the study of the performances in sodium half-cell of a SnSb particles dispersion over a carbonaceous matrix. Xiao et al. obtained a reversible alloying of Na and a stable capacity of ~400 mAh g^{-1} [19].

Transition metal oxides (MO_x with M = Fe [20], Co [21], Cu [22]), with electrochemical active transition metal ions, have drawn the attention as possible low cost and easy-to-manufacture SIB conversion anode materials. Their reactivity, electrochemical performances, and effects of morphology and structural properties on lithium storage, have been widely analyzed. On the contrary, same type of studies related to reactivity with Na, remain poorly explored. The study of Na reactivity with spinel Co_3O_4 nanoparticles has been recently reported by few groups, and a first understanding of the possible undergoing conversion mechanism has been hypothesized.

The general reaction proposed for the sodium reactivity with spinel type oxides and other conversion materials is the following [11]:

$$MO_x + 2xNa^+ + 2xe^- \rightarrow xNa_2O + M$$

Notable aspects of the reaction above reported are its reversibility and the theoretical capacity of oxides (>600 mAh g^{-1}), considerably higher if compared to carbonaceous materials or intercalation materials for which capacity is limited by the number of available sites for Na^+ insertion [6](~300 mAh g^{-1}). Spinel Co_3O_4, thanks to its high theoretical capacity (~890 mAh g^{-1}), has aroused, since the early stages of LIB technology development, a great interest as a high capacity conversion anode material [21,23,24]. Along with the advantage of having a high theoretical capacity comes also the challenge represented by the large particle volume variation during sodiation which leads rapidly to a considerable fade in material properties. In a recent work by Sun et al. a Co_3O_4 porous particles/graphene compound has been investigated as active anode material in a sodium ion battery [25]. The hybrid compound ensured a good capacity (~500 mAh g^{-1}) and good cycle stability at the current density of 25 mA g^{-1}. Owing to the volume variation connected to conversion mechanism, morphology of active material particles acquires a primary importance. Crystal shape, exposed facets, hierarchical structures and porosity of particles are essential features to be taken into consideration when it comes to minimize the deleterious effect of excessive volume change induced stresses. Effect of different morphology of Co_3O_4 particles over the electrochemical performances has been highlighted in the case of lithium batteries, and the better performances of polycrystalline hierarchical structure compared to single nanocrystals has been confirmed [26]. Another negative aspect related to conversion materials is the irreversible capacity involved in the first charge/discharge loop. It determines a significant drop in the residual capacity available for the following cycles. By many, this behavior has been addressed to the SEI formation which involves a non-negligible amount of active species.

In the present work, three different morphologies of spinel Co_3O_4 have been prepared. These have been synthesized using facile and easily scalable synthetic routes and they have been deeply investigated under the electrochemical point of view as anode materials in metallic sodium half-cells; conclusions related to the morphology influence have thus been made. Moreover, the characteristic conversion mechanism beyond the electrochemical reaction with sodium has been studied. Finally, the problem related to the first cycle irreversible capacity has also been tackled. In particular, the effect of a chemical pre-sodiation of the Co_3O_4 electrode has been taken into consideration.

2. Experimental

2.1. Synthesis

Hydrothermal synthesis technique is known to be a versatile synthetic route that allows to obtain a large variety of different morphologies by changing operating conditions, namely temperature, volume (fill factor), hydrothermal step time, precursor and capping agents concentration and pH [24,26]. In studying spinel Co_3O_4 morphology effects over the electrochemical behavior, several structures have been prepared and tested. In this work, the preparation and characterization of just the three most significant ones, according to their electrochemical performances, are reported. The three samples are here listed with their codes: CO_S (cobalt oxide slabs), CO_N (cobalt oxide needles), CO_F (cobalt oxide flakes). All the chemicals were of analytical grade and were used as received. The cobalt precursor, $Co(NO_3)_2 \cdot 6H_2O$ (ACS reagent, ≥98%, Sigma-Aldrich®) has been dissolved in deionized water together with $CO(NH_2)_2$ (ACS reagent, Sigma-Aldrich®), used as a mineralizing agent, and the solution has been transferred to a 100 mL Teflon-lined stainless steel autoclave. The autoclave has been heated starting from room temperature using a heating rate of 4° min^{-1}, and after dwelling at the set-point temperature (according to the synthetic route) it has been let to cool down naturally to room temperature again. The operational parameters for the three samples mentioned above are reported in Table 1. After the hydrothermal step the intermediate was collected by centrifugation from the autoclave, washed several times with deionized