A Na$^+$-storage electrode material free of potential plateaus and its application in electrochemical capacitors

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ABSTRACT

The need of large-scale energy storage calls for the application of environmentally benign and economic sodium storage electrode materials. At present, most of the existing positive electrode materials for Na$^+$-storage demonstrate many small plateaus, which are a disadvantage for the practical application. We found that some inert elements like Al can straighten the charge–discharge curves and stable the structure of the positive electrode materials. Here we synthesized positive electrode material of Na$_{0.67}$[Mn$_{0.75}$Al$_{0.25}$]O$_2$ by the spray drying method. This positive electrode material was matched with the negative electrode material of activated carbon to assemble a Na$^+$-capacitor. This capacitor can retain 90% of capacity after 1000 charge–discharge cycles. The advantage of the Na$^+$-capacitor in properly assessing the cycle performance of the positive electrode material has been specially pointed out. Moreover, the Na$^+$-capacitor possesses higher volumetric energy and power densities than electric double-layer capacitors.

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1. Introduction

Na$^+$-storage electrode materials have been discovered for some decades [1–9], nonetheless, their progress in practical application was too tardy to keep the pace with those of Li$^+$ storage. At the beginning of this century, works related to Na$^+$-storage electrode materials were rather sparse. From 2008, inspired by the wave of new energy sources, the search for energy storage in a large scale has become a global issue and the research interest on Na$^+$-storage electrode materials got revived. However, it is still a long march before accomplishing the practical application of Na$^+$-storage electrode materials and related devices. Comparing with Li$^+$-storage ones, Na$^+$-storage devices possess either advantages or disadvantages, depending on which aspect to be preferred [3,10]. At present, most of the Na$^+$-storage electrode materials inherit from their corresponding Li$^+$-storage ones, but mainly differs by the alkali cation as the charge carrier [2]. In fact, the replacement of Li$^+$ by Na$^+$ in electrode materials can't save much cost since the alkali elements only amount to very low portions inside. The major economical contribution may come from the electrolyte solutions. Therefore, the electrochemical performance of Na$^+$-storage electrode materials must be competitive enough at first. For this purpose, designing brand new electrode materials of Na$^+$ storage has become a choice [10–12]. However, before the emerging of new ones, screening and optimizing the available Na$^+$-storage electrode materials are practical strategies. So far, both the negative and positive electrode materials of Na$^+$ storage are far less mature than those Li$^+$-storage ones. Fortunately, the negative electrode side for Na$^+$-storage has made some promising achievements [11–21]. In contrast, it is still a hard work to develop satisfactory positive electrode materials [22–36]. Up to now, sodium transitional metal oxides with layered structures occupy the lion's share in this field maybe due to their acceptable specific capacities and rate capabilities. There can be various choices of the transitional metals, like Co, Ni, Mn, Fe, Cr and V, and numerous modifications by metals doping. Within these oxides, the layered structures containing Mn constitute the most prominent family of Na$^+$-storage electrode materials by virtue of the low cost, abundance and environmental benignity of their raw materials. However, the bigger size of Na$^+$ increases the lattice energy and retards its transport as compared with Li$^+$ [3]. Consequently, the charge–discharge curves of these oxides display too many small potential plateaus [22,23,27,35], which stands for multiple phase changes. These phase changes will cause successive distortions and strains in the crystal structures of oxides and thus deteriorate their electrochemical performance. One of the effective ways to smooth away these potential plateaus is to substitute some parts of Mn with other metals like Co, Ni and Fe [37–38]. In this study, we attempted to dope the inert element of Al into sodium manganese oxides since it can form strong bonds with oxygen and stabilize the layered structures of oxides [39]. Of course, Al doping will inevitably decrease the Na$^+$ storage capacity of the electrode material, which looks like a drawback. But we believed that its appointment in a fitful Na$^+$-storage device becomes the key issue here.

Recently, we have developed non-aqueous Na$^+$-capacitors using sodium titanate as the negative electrode [14–15]. These studies motivated our interest to apply Na$^+$-storage electrode materials in electrochemical

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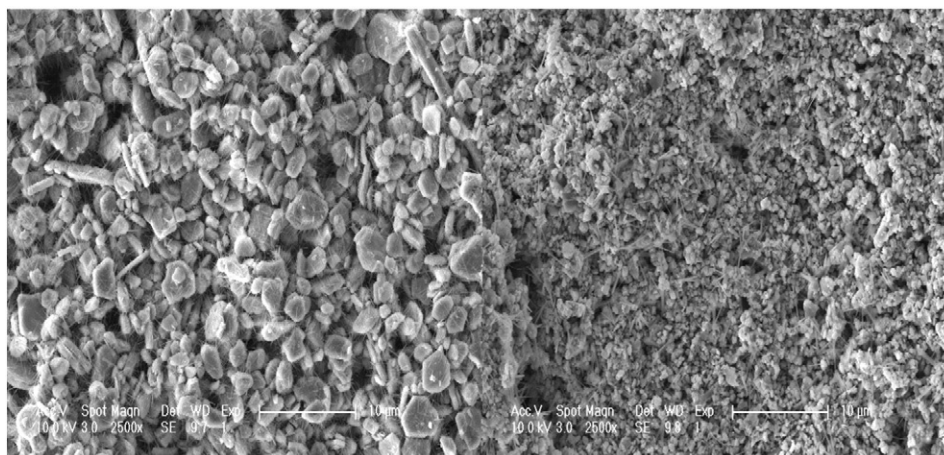 *E-mail address:* hongyuwang@ciac.ac.cn (H. Wang).

Fig. 1. SEM image of $Na_{0.67}MnO_2$ (left) and $Na_{0.67}[Mn_{0.75}Al_{0.25}]O_2$ (right).

capacitors. There are at least three reasons. First, Na^+-storage electrode materials generally deliver smaller capacity values than their corresponding Li^+-storage ones. This fact will somehow worsen the competitive role of Na^+-storage electrode materials in secondary batteries calling for high energy density. But in electrochemical capacitors tolerant for smaller capacity, the Na^+-storage electrode materials can find many chances. Second, the apparently bigger size of Na^+ incurs its slower transport inside the bulk electrode materials. As a result, Na^+-storage electrode materials are usually manufactured into nano-sized architectures to avoid this shortcoming. The nano-structured Na^+-storage electrode materials will contribute considerable "pseudo-capacitive" capacity values [15]. Third, Na^+-capacitors may be a reliable platform to properly evaluate the performance of Na^+-storage electrode materials. In most of the current electrochemical tests, sodium metals are always employed as the both counter and reference electrodes in half cells. Since sodium metal is much more chemically active than lithium metal, the interfacial stability between sodium metal electrode and electrolyte solutions may be problematic, which will obscure the correct expressions of half cells in accessing Na^+-storage electrode materials. For instance, the cycle-ability of these half cells could be limited by sodium metal electrodes instead of the target electrodes. In contrast, the counter electrodes in Na^+-capacitors can be flexibly selected. For instance, graphite and activated carbon (AC) can fulfill this task [14–15]. In this study, AC was

coupled with the Na^+-storage metal oxides to construct Na^+-capacitors. Here AC acts as the negative electrode, which principally involves the physical adsorption of Na^+ ions during charge storage process [40–42], while the sodium manganese oxides work as the positive electrodes. The effect of Al doping on the performance of Na^+-capacitors has also been addressed.

2. Experimental

2.1. Electrode materials

For preparing the Al-doped sodium manganese oxide sample, 36.9 g $MnAc_2 \cdot 4H_2O$, 15 g $Al(NO_3)_3 \cdot 9H_2O$, 5.33 g NaOH and 42 g citric acid were dissolved into 500 ml pure water and mixed homogeneously. This solution was dried at 180 °C by spraying. The dry powder was calcined at 900 °C for 6 h and this process was repeated for 2–3 times. Then the positive electrode material with the nominal composition of $Na_{0.67}[Mn_{0.75}Al_{0.25}]O_2$ was obtained. Another positive electrode material without Al-doping, namely, $Na_{0.67}MnO_2$ was prepared by similar procedures with $MnAc_2 \cdot 4H_2O$ and NaOH as the starting materials.

The negative electrode material was AC (PW15M131, Kureha Co. Ltd.), some of its details can be found in [43].

2.2. Electrochemical measurements

The cell assembling was conducted in glove-box. AC was set as the negative and the metal oxides were taken as the positive electrode materials. The weight ratio of the negative to positive electrode materials was 1.5. The electrolyte solution was 1 M $NaClO_4$ dissolved in PC and the current collector was aluminum mesh. Other details about cell assembling were the same as those in [43]. In a half cell, sodium metal was used as the negative electrode. In a three-electrode cell for electrochemical studies like cyclic voltammetry (CV) and impedance spectroscopy (IS), the quasi-reference electrode (QRE) was fabricated by an excess amount of activated carbon. Its reliability and safety have been adequately tested in the past studies [44–46]. The potential values of an electrode versus AC-QRE and sodium metal differs by about 2.73 V. Unless otherwise specified, all these electrochemical tests were performed at about 20 °C.

3. Result and discussion

Fig. 1 exhibits the SEM images of $Na_{0.67}MnO_2$ and $Na_{0.67}[Mn_{0.75}Al_{0.25}]O_2$ samples. Although they were processed according the same flow, their morphologies are quite different. $Na_{0.67}MnO_2$ particles are typically plates with the wider dimension of several micrometers,
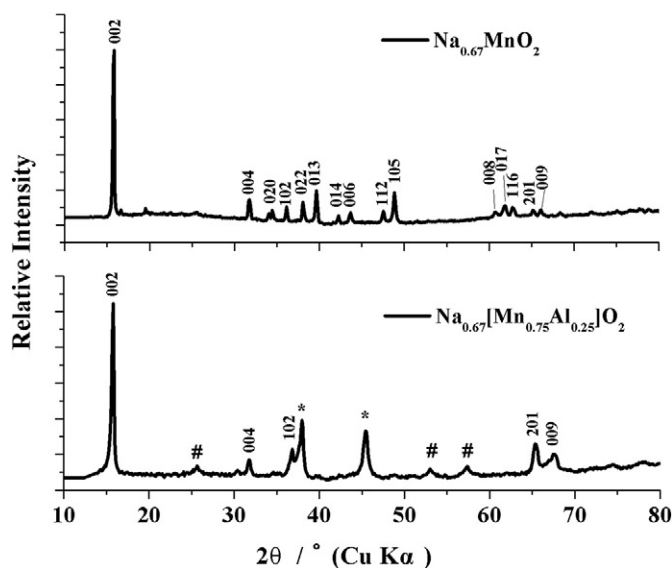

Fig. 2. The powder XRD patterns of $Na_{0.67}MnO_2$ and $Na_{0.67}[Mn_{0.75}Al_{0.25}]O_2$. "*" Stands for the characteristic peaks of $NaAlO_2$; "#" stands for the characteristic peaks of Al_2O_3.