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Bi-metal organic framework derived nickel manganese oxide spinel for lithium-ion battery anode

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ABSTRACT

Ternary transition metal oxides offer several advantageous features compared to the binary analogs due to presence of hetero transition metals with multiple valence states and the possible synergistic effects. Recently, metal organic frameworks have emerged as exotic template for synthesis of morphologically pre-designed metal oxide nanostructures. Nonetheless, synthesis of heteroatom ternary metal oxides through bi-metal organic framework (BMOF) route has proved to be challenging. Herein, we report a scalable single-step synthesis protocol for obtaining Ni/Mn-1,3,5-benzenetricarboxylate BMOF from which interconnected multi-faceted particles of $NiMn_2O_4$ spinel could be derived by thermal calcination at 800 °C. When applied as an anode for lithium-ion battery, the BMOF-derived mesoporous $NiMn_2O_4$ delivered a high reversible capacity (1049 mAh g^{-1}), good rate performance (413 and 258 mAh g^{-1} at 503 and 1257 mA g^{-1}) and good electrochemical stability highlighting the MOF-derived morphological advantages. The present results would help designing ternary metal oxide nanostructures for electrochemical energy storage application.

1. Introduction

Conventional lithium-ion battery (LIB) technology, based on Li interaction ability of graphitic anode, proves to be insufficient to meet the desired level of energy/power densities and the stringent safety requirements for emerging applications like automobile electrification or grid-scale energy storage [1–6]. Thus, it is imperative to look for alternative anode materials. In this quest, transition-metal oxides (TMOs) have emerged as the most promising anode materials for their high capacity and better safety owing to the reversible conversion reactions of transition metal and lithium oxide [7,8]. Following the first report by Tarascon et al., extensive work has been performed on various binary transition metal oxides such as TiO_2, V_2O_5, Cr_2O_3, Mn_2O_3, Mn_3O_4, CoO, Fe_2O_3, Co_3O_4, Fe_3O_4, NiO etc. [9–12], and mixed binary transition metal oxides [13,14]. Recently, developing nanostructures of ternary transition-metal oxides (TTMOs) of spinel-like structures with hierarchical mesopores has been demonstrated as an efficient strategy to deliver high specific capacities due to presence of two transition metals with multiple valence states and the possible synergistic effects [15–19]. For example, Zhu et al. have achieved high reversible lithium storage capacity of 930 mA h g^{-1} at a current density of 200 mA g^{-1} after 200 cycles for two-dimensional ultrathin $ZnCo_2O_4$ nanosheets [15]. Good electrochemical performances have also been achieved for $ZnFe_2O_4$ [16], porous $CoFe_2O_4$ [17], carbon supported $CuCo_2O_4$ [18], and graphene anchored $CoMn_2O_4$ [19]. It is observed that bi-component binary/ternary TMOs showed enhanced performances compared to the individual components [20–25], e.g., MOF derived porous ZnO/$ZnFe_2O_4$ hybrid nanostructures [20], CoO/$CoFe_2O_4$ [21], MOF derived hierarchical $NiFe_2O_4$/Fe_2O_3 nanotubes [22], hierarchical mesoporous hybrid NiO-$MnCo_2O_4$ microspheres [23], ultrathin NiO/$NiFe_2O_4$ nanoplates decorated graphene nanosheets [24], Mn_2O_3/$NiMn_2O_4$ hollow microspheres [25] etc. The above studies demonstrate the importance of developing ternary TMOs as anodes for high energy density LIB. Among the AB_2O_4 type spinel oxide family, $NiMn_2O_4$ could be a promising electrode material from the molecular structure and crystallographic aspects, apart from its high chemical stability and good theoretical capacity (~922 mAh g^{-1}, considering $8e^-$ transfer process) [26]. In this cubic inverse spinel, the nickel cations occupy the octahedral B-sites in preference to the tetrahedral A-sites of the cubic close packed oxygen sub-lattice while the manganese cations are distributed in both tetrahedral A-sites and octahedral B-sites [27–29]. As a result, $NiMn_2O_4$ is expected to offer large numbers of redox active sites for superior electrochemical performance. However, the first investigation did not produce encouraging result where $NiMn_2O_4$ shows a rapid capacity fading with a specific capacity of only 220 mAh g^{-1} after 20 cycles [30]. In an effort to arrest the capacity fading by improving the charge transport kinetics, various research groups have tried making composite with carbon [26], and metal ion doping [31,32]. Ma et al.

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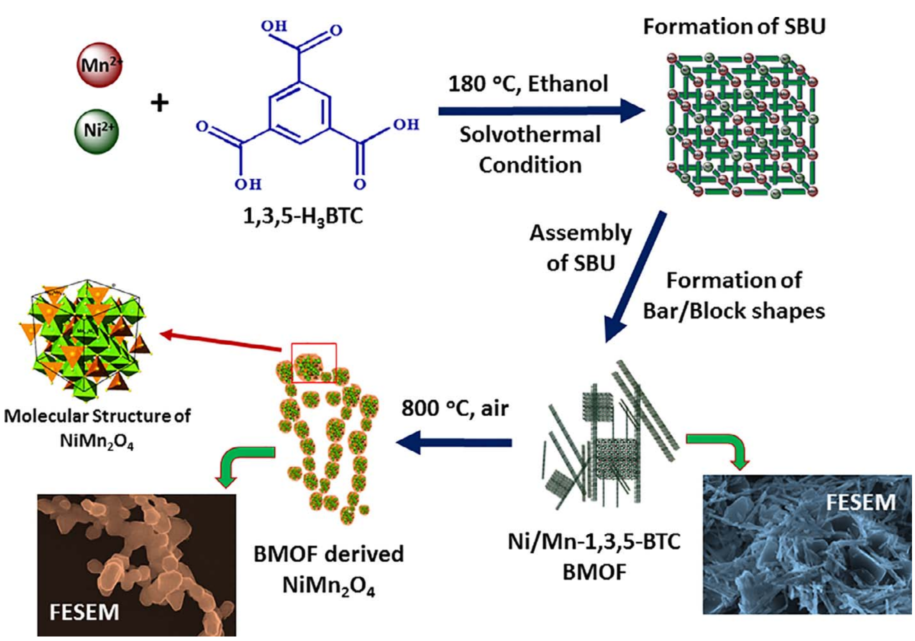

Scheme 1. Schematic representation for the synthesis of BMOF derived $NiMn_2O_4$.

have obtained a capacity value of 620 mAh g^{-1} at a current density of 200 mA g^{-1} after 250 cycles for Fe doped $NiMn_2O_4$ [31]. It is well known that morphology and microstructure of the active materials play a crucial role for electrochemical stability and enhanced performance [11,20,33,34]. In this respect, recently, metal organic framework (MOF) derived synthesis of metal oxides have emerged as an attractive route to obtain predesigned geometrical morphology, faceted crystals, regular channels and pores which altogether act synergistically to deliver promising electrochemical performance [20,33–35]. MOFs, constructed of metal ion clusters and organic linkers, offer the possibility of obtaining metal oxides thereof with pre-designed morphology as different organic linkers have different geometrical coordination ability with the metal nodes depending on the symmetry of the linker and coordination preference of the metal ion. Since combination of a particular metal ion with a particular organic linker will always lead to formation of same morphological features, metal oxides synthesized by MOF *exo*-templating route will have a higher degree of reproducibility compared to other synthetic routes based on solid state, combustion, wet chemistry etc. However, synthesis of mixed-metal MOF with more than one transition element within the same structure is proved to be challenging [33,35]. Until now, there is no report on the electrochemical properties of MOF derived $NiMn_2O_4$ though there is a report on synthesis of $NiMn_2O_4$ from $(NiMn_2)\{C_6H_3(COO)_3\}_2$ where the MOF was prepared in two steps by partial replacement of octahedral Mn^{2+} by Ni^{2+} ions of pre-synthesized monometal MOF, $(Mn_3)\{C_6H_3(COO)_3\}_2$ using 1,2,4-benzenetricarboxylic acid as organic linker [36]. In the present work, we have successfully synthesized Ni/Mn-1,3,5-benzenetricarboxylic BMOF in one step by a simple solvothermal process by using 1,3,5-benzenetricarboxylic acid as the organic linker and obtained $NiMn_2O_4$ by calcination of the BMOF. The BMOF derived $NiMn_2O_4$, thus obtained, has been tested as anode for lithium-ion battery in the pristine form to understand exclusively the effect of MOF induced morphology on the electrochemical stability.

2. Experimental

2.1. Materials

The following chemicals were used as precursors for the synthesis: $Ni(NO_3)_2{\cdot}6H_2O$ (99%, Acros organics, India), $Mn(NO_3)_2{\cdot}4H_2O$ (98 + %, Acros Organics, USA), trimesic acid (1,3,5-H_3BTC, ~95%, Merck, Germany), and ethyl alcohol (C_2H_5OH) (99%, Merck, Germany).

2.2. Synthesis of Ni/Mn-1,3,5-benzenetricarboxylic BMOF (Ni/Mn-1,3,5-BTC BMOF)

Ni/Mn-1,3,5-BTC BMOF was synthesized via a simple solvothermal method in a 500 mL closed glass vessel container. Initially, 1.165 g (4.0 mmol) of $Ni(NO_3)_2{\cdot}6H_2O$ and 0.94 g (3.75 mmol) of $Mn(NO_3)_2{\cdot}4H_2O$ were dissolved in 50 mL of C_2H_5OH under constant stirring (solution-A). Then, another solution was prepared by dissolving 0.875 g (4.16 mmol) of trimesic acid (1,3,5-H_3BTC) in 30 mL of C_2H_5OH (solution-B). Solution-A was slowly added to solution-B under constant stirring and the resulting solution was transferred to a glass vessel. The reaction was performed in closed conditions by keeping the glass vessel on a hot plate at 140 °C for 4 days under autogenous pressure. The obtained synthesized powder (Ni/Mn-1,3,5-BTC BMOF) was centrifuged, washed repeatedly with ethanol to remove any residual metal ions and finally, dried at 120 °C for 12 h in an air oven.

2.3. Synthesis of BMOF derived $NiMn_2O_4$

$NiMn_2O_4$ was synthesized via calcination of Ni/Mn-1,3,5-BTC BMOF precursor in an air-furnace at 800 °C for 6 h with a heating rate of 2 °C per minute. The calcination temperature was determined based on the phase diagram of the NiO-Mn_2O_3 system [37] and the thermal stability window of $NiMn_2O_4$ [29,38]. The synthesized product was kept inside a vacuum desiccator until further use. A schematic representation of the synthesis process is shown in Scheme 1.

2.4. Material characterization

Powder XRD patterns of the synthesized Ni/Mn-1,3,5-BTC BMOF and BMOF derived $NiMn_2O_4$ were recorded in the 2θ range 5°–90° at a scanning rate of 2° min^{-1} by an X-ray diffractometer (Philips X'Pert, the Netherlands) with a Cu-Kα radiation at 40 kV and 40 mA. Thermal stability of 1,3,5-H_3BTC and synthesized Ni/Mn-1,3,5-BTC BMOF were investigated by thermogravimetric analysis (TGA) in the temperature range 30–1000 °C in air at a heating rate of 10 °C min^{-1} using Simultaneous Thermal Analyzer (STA449F, Netzsch, Germany). FTIR spectra of 1,3,5-H_3BTC and synthesized Ni/Mn-1,3,5-BTC BMOF were recorded in the wave number range 4000–400 cm^{-1} using a BOMEN