

Porous manganese oxide nanocubes enforced by solid electrolyte interphase as anode of high energy density battery



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ABSTRACT

We present a novel configuration for stabilizing manganese oxide as anode of high energy density lithium ion battery. Porous Mn₂O₃ nanocubes were developed with cubic MnCO₃ as precursor and coated with a solid electrolyte interphase (SEI) by applying an electrolyte additive, prop-1-ene-1,3-sultone (PES). Discharge-charge tests demonstrate that the resulting anode exhibits excellent cyclic stability. Electrochemical and physical characterizations indicate that PES is easily reducible on Mn₂O₃ forming a protective SEI, which maintains the structural integrity of Mn₂O₃ particles. The porosity of the cubes and the SEI on the particles co-contribute to the improved cyclic stability of the resulting anode.

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1. Introduction

Lithium ion battery has been widely used in small electronic devices because of its superior advantages including no memory effect and longer cycle life, compared with other secondary batteries [1–6]. However, for the large-scale applications such as electric vehicles, the energy density of lithium ion battery needs to be improved further. The energy density limitation of currently available lithium ion battery results from the lower specific capacity of cathodes based on layered LiCoO₂, spinel LiMn₂O₄ and olivine LiFePO₄, and anode based on graphite that has only 372 mAh g⁻¹. Therefore, a great deal of interest is created in seeking alternative electrode materials with higher specific capacity [7–11].

Metal oxides (M_xO_y, M = Mn, Co, Sn, etc.) are appealing anodes because they can provide a far larger specific capacity than graphite [12–15]. Among these oxides, Mn₂O₃ is the most promising due to its unique features including high theoretical capacity (1018 mAh g⁻¹), resource abundance and environment benignity [16–18]. However, Mn₂O₃ exhibits poor cyclic stability

due to the drastic volume change and the severe pulverization of Mn₂O₃ particles during cycling, which is universal for the electrode materials with high specific capacity.

Porous materials with nanosize particles have been constructed to improve the cyclic stability of the electrode materials with high specific capacity, since the pores provide the materials with spaces to buffer the volume changes, facilitating the cyclic stability of the materials [19–21]. However, the improvement in cyclic stability from volume buffering is unsatisfactory because the porous structure will be ruined finally due to the periodical volume change of nanoparticles during the extended cycling [22,23]. Additionally, the porous structure increases significantly the contact area, leading to the severe dissolution of metal ions in electrode materials and the decomposition of electrolyte on electrodes [24].

Coating metal oxides with structurally stable inorganic compounds is usually adopted for the cyclic stability improvement of metal oxides, because the coating layer not only confines the volume change of the oxide but also separates the oxides from direct contact with the electrolyte, reducing the metal ion dissolution and the electrolyte decomposition [25–28]. For instance, the cyclic stability of porous cubic Mn₂O₃ has been successfully improved by coating Mn₂O₃ with TiO₂ [16]. Since the TiO₂ coating is rigid structurally, it can be named as hard coating. Apparently, the procedure for hard coating is complicated and it is

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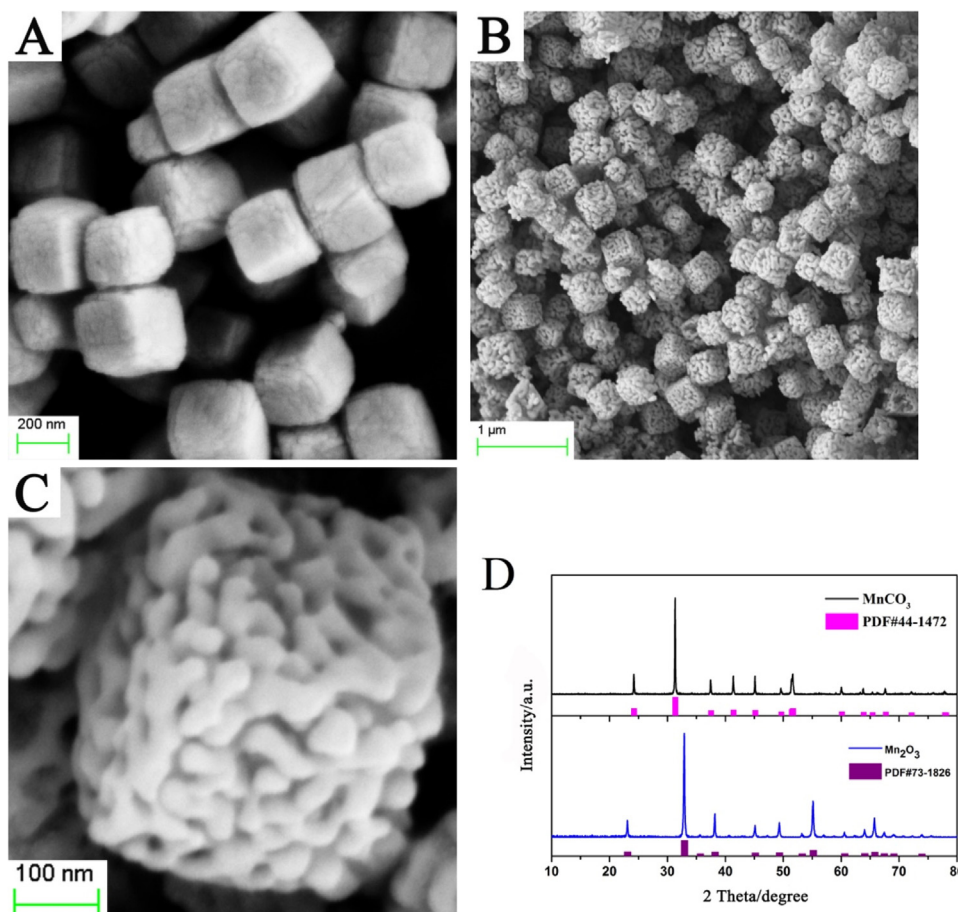


Fig. 1. FESEM images of MnCO_3 nanocubes (A) and porous Mn_2O_3 nanocubes (B–C); XRD patterns of MnCO_3 and porous Mn_2O_3 nanocubes (D).

difficult to achieve a uniform coating layer on the particles of metal oxides.

Similarly to the contribution of hard coating, solid electrolyte interphase (SEI) formed by applying electrolyte additive also provides a protection for electrode materials, anodes or cathodes, leading to the improved cyclic stability of the electrode materials [29–32]. Since the interphases are composed of the polymer products from the oxidation or reduction of electrolyte additives, which are flexible, they can be named as soft coating. Soft coating is performed by applying an electrolyte additive into electrolyte and formed during the initial charge/discharge processes, therefore it is more easily performed and more uniform coating layer can be achieved by soft coating than hard coating.

In fact, the successful application of graphite anode in commercialized lithium ion battery depends to a great extent on the SEI, which is usually formed by vinylene carbonate (VC) and propane sultone (PS) [33,34]. With the SEI available, graphite anode can be protected from the exfoliation of layered structure, which is caused by the co-intercalation of carbonate solvents with lithium ions. The protection effectiveness of the SEI is related to the preference in reduction activity of the electrolyte additives. To avoid the co-intercalation of solvents, the electrolyte additives should be reduced preferentially to the electrolyte.

In our previous reports, we found that prop-1-ene-1,3-sultone (PES) could be reduced preferentially to PS on graphite and was more effective as an electrolyte additive for the cyclic stability improvement of graphite anode than PS [35]. The reduction peak potential in cyclic voltammograms for PES on graphite is 1.2 V (vs. Li^+/Li), which is higher than that for PS (0.75 V) and the potential for the co-intercalation of solvent (1.0 V), yielding the better

contribution of PES than PS to the cyclic stability of graphite anode. With this knowledge and considering that the potential for lithium intercalation in Mn_2O_3 is lower than 1.0 V, we proposed in this work a new approach for the cyclic stability improvement of Mn_2O_3 , in which soft coating was achieved through forming an SEI derived from the preferential reduction of PES as an electrolyte additive. The effectiveness of this soft coating was evaluated with charge/discharge tests and the related mechanisms were understood by electrochemical measurements and physical characterizations. It was found that the formed SEI could maintain the

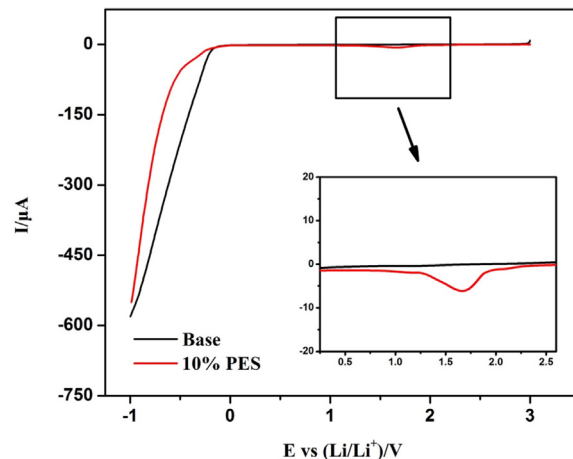


Fig. 2. Voltammograms of Pt electrode in $1 \text{ mol L}^{-1} \text{ LiPF}_6\text{-EC:DMC (1:2, V/V)}$ without and with 10 wt% PES at 1.0 mV s^{-1} .

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