Synthesis of $ZnMn_2O_4$ tubular array anode materials for an efficient lithium ion storage electrode

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One-dimensional nanostructures such as nanowires, nanorods, nanobelts, and nanotubes have been extensively exploited as an alternative electrode platform in rechargeable Li-ion battery system because they can offer direct channels for the enhanced charge transport and accommodate strain energy effectively during repeated charge/discharge cycles.[1,2] However, the aggregation of nanomaterials leads to disturbance of mixing with nano-structured active materials and dispersants, which could decrease the cycling stability during charge/discharge cycles. Also, the ancillary materials, including conductive agents and polymeric binders, can lower the energy density of the electrode in the traditional electrode preparation methods.[3,4] Therefore, directly grown arrays of one-dimensional nanostructures on current collectors have drawn interests for the development of alternative anode materials in Li-ion battery.

In this research, we report a $ZnMn_2O_4$ tubular array structure, which was directly synthesized on titanium current collectors for an efficient lithium ion storage electrode. The $ZnMn_2O_4$ tubular array structures were prepared by reactive template approach combined with calcination process. The as-synthesized $ZnMn_2O_4$ tubular arrays were well-oriented on the current collector (Figure 1), which can prevent the aggregation of the grown arrays each other. The lithium storage performance of the as-prepared $ZnMn_2O_4$ tubular arrays was explicitly demonstrated by applying them to working electrode without additive materials. The $ZnMn_2O_4$ electrode exhibited excellent initial discharge capacity of 1198.3 mAh g^{-1}, and it also showed higher cycling stability over 100 cycles at a current density of 100 mA g^{-1} between 0.01 V and 3.0 V (Figure 2). We hypothesize that the improved cycling stability of $ZnMn_2O_4$ tubular array electrode might be induced from the internal hollow cavities and spaces between the neighboring tubular arrays, which could accommodate strain energy efficiently during repeated cycling. Furthermore, directly grown $ZnMn_2O_4$ tubular arrays could reduce the nanoparticle agglomeration or pulverization during cycling, which results in excellent capacity-retentions. In summary, we believe that the novel $ZnMn_2O_4$ tubular array architectures can be a powerful candidate for a lithium storage electrode platform.

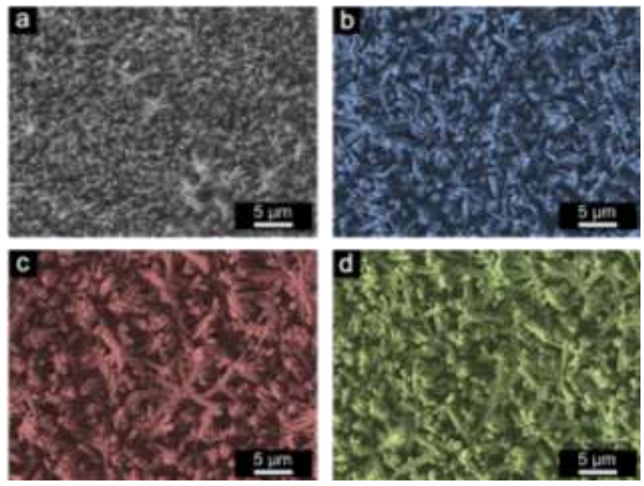

Figure 1. Typical SEM images of the (a) ZnO nanorods and the $ZnMn_2O_4$ tubular arrays synthesized at (b) 24 h, (c) 48 h, and (d) 72 h reaction time.

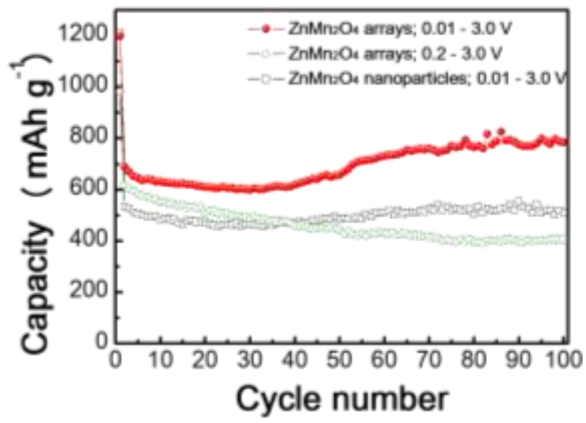

Figure 2. Discharge capacity-cycle number curves of $ZnMn_2O_4$ tubular arrays in the potential window, 0.01–3.0 and 0.2–3.0 V at a current density of 100 mA g^{-1}, and of $ZnMn_2O_4$ nanoparticles at a current density of 100 mA g^{-1} between 0.01 and 3.0 V.

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Acknowledgement

This work was supported by the National Research Foundation (NRF) grant funded by the Ministry of Education, Science and Technology of Korea (MEST) (No. 20110016600) and by the Global Frontier R&D Program (0420-20120126) on Center for Multiscale Energy System through NRF. We also appreciate the financial support by Korea government Ministry of Knowledge Economy (No. 20103020030020-11-2-200) and by the Core Technology Development Program from the Research Institute of Solar and Sustainable Energies (RISE/GIST).