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Nanastructured $H_2Ti_8O_{17}$ Nanoarrays as Three-Dimensional Anodes for Lithium-ion Batteries

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Lithium-ion batteries (LIBs) with prominent advantages of high energy and power density as well as long cycling life have now shown that they have a promising future in the coming era of hybrid electric vehicles (HEVs) and electric vehicles (EVs).[1,2] However, the commercialization of LIB based electric vehicles has proceeded slower than projected, partially due to two pertinent technical challenges facing the commercial carbon based anode materials (typically graphite), particularly: (i) unstable SEI formed on graphite below might lead to low columbic efficiency; and (ii) safety concerns arising due to lithium dendrite formation which occurs because of the low Li-intercalation potential of graphite approaching 0 V (*vs* Li/Li^+).[3,4] Furthermore, at high charge-discharge rates, the slow Li^+ diffusion in the graphite anode materials will be a source of large polarisation, resulting in decrease power density and effectively limiting the practical application in commercial HEVs/EVs. Being inherently safe and chemically compatible with the electrolyte, titanium (Ti) based materials (anatase TiO_2, TiO_2-B, $Li_4Ti_5O_{12}$) with high operating voltages (> 1 V *vs* Li/Li^+) that ensure improved safety are considered the most promising alternatives to the conventional anode materials used in LIBs. Among the Ti-based compounds investigated, TiO_2-B has emerged as a promising candidate boasting a high theoretical capacity of 335 mA h g^{-1}.[5] On other hand, Idemoto *et al*. recently reported the use of $H_2Ti_{12}O_{25}$ as novel anode materials for LIBs, and depicted a higher capacity of 225 mA h g^{-1} compared to $Li_4Ti_5O_{12}$ (175 mA h g^{-1}) with excellent cycling performance.[6] This successfully illustrated the promise of using hydrogen titanium oxides (HTO) as a new class of anode materials for LIB applications.

In the present work, we have successfully synthesized single crystalline $H_2Ti_2O_5$, $H_2Ti_8O_{17}$, TiO_2-B and anatase TiO_2/TiO_2-B nanowire arrays directly on a flexible Ti foil. Prepared by subjecting $H_2Ti_2O_5 \cdot H_2O$ to heating at different temperatures, these nanowires have average diameters of 74 nm and lengths of around 15 μm. For the first time, the electrochemical Li ion insertion/extraction properties of these 3D single crystalline HTO and titanium oxide nanowire array anodes have been characterized, providing a gauge of their practical applicability towards LIBs. The prepared $H_2Ti_8O_{17}$ nanowire based electrode demonstrated optimal performance through direct testing as an anode in a half cell LIB, providing high charge/discharge capacities, excellent rate capabilities and exemplary cycling performance. Specifically, reversible Li insertion and extraction reactions around 1.6-1.8 V with initial intercalation capacities of 326 and 271 mAh g^{-1} at a cycling rate of 0.1 C (where 1 C=335 mA h g^{-1}) were observed for $H_2Ti_8O_{17}$ and TiO_2-B nanowire arrays, respectively. Among the four compounds investigated, the $H_2Ti_8O_{17}$ nanowire electrode demonstrated optimal cycling stability, delivering a high specific discharge capacity of 157.8 mA h g^{-1} with a coulombic efficiency of 100% even after the 500th cycle at a current rate of 1 C. Furthermore, the $H_2Ti_8O_{17}$ nanowire electrode displayed superior rate performance with rechargeable discharge capacities of 127.2, 111.4, 87.2 and 73.5 mA h g^{-1} at 5 C, 10 C, 20 C and 30 C, respectively. These results present the potential opportunity for the development of high-performance LIBs based on nanostructured Ti-based anode materials in terms of high stability and high rate capability.

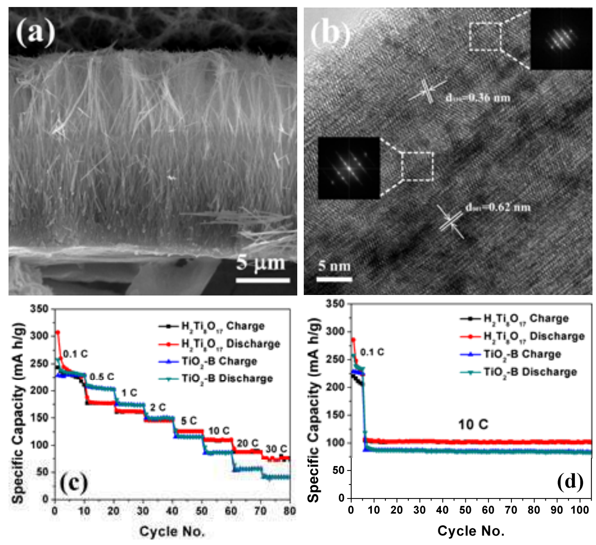

Figure 1. SEM image (a), HRTEM image (b) of $H_2Ti_8O_{17}$ nanowire, and electrochemical performance of TiO_2-B and $H_2Ti_8O_{17}$ nanowire electords.

References

1. P. G. Bruce, B. Scrosati and J. M. Tarascon, *Angew. Chem. In. Ed.*, 2008, **47**, 2930-2946.
2. L. W. Ji, Z. Lin, M. Alcoutlabi and X. W. Zhang, *Energy Environ. Sci.*, 2011, **4**, 2682-2699.
3. G. N. Zhu, Y. G. Wang and Y. Y. Xia, *Energy Environ. Sci*., 2012, **5**, 6652-6667.
4. L. F. Cui, Y. Yang, C. M. Hsu and Y. Cui, *Nano Lett.*, 2009, **9**, 3370-3374.
5. S. H. Liu, H. P. Jia, L. Han, J. L. Wang, P. F. Gao, D. D. Xu, J. Yang and S. N. Che, *Adv. Mater.*, 2012, **24**, 3201-3204.
6. J. Akimoto, K. Chiba, N. Kijima, H. Hayakawa, S. Hayashi, Y. Gotoh and Y. Idemoto, *J. Electrochem. Soc.*, 2011, **158**, A546-A549.