

New Silicon and Titanium Boride Nanocomposite Anodes for Li-Ion Batteries

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INTRODUCTION

Lithium-ion batteries have been the focus of intense study over the last two decades and both cathode and anode materials have been intensely researched. In the area of anodes, there has been considerable work to search for alternative materials to graphite, which has been the customary anode material of choice. Silicon and tin are potentially attractive candidates but have severe limitations due to the large volume induced stresses. The concept of embedding these in inactive materials has been actively pursued.

We have recently shown the potential of Si/TiN active/inactive nanocomposite synthesized using high-energy mechanical milling (HEMM) as an anode material. As reported, materials with good electrical conductivity, mechanical strength and chemical inertness are desirable to act as effective inactive matrices. Titanium boride having similar properties to titanium nitride, could act as a good matrix. It was therefore decided to explore the concept of active-inactive nanocomposite anode systems further using silicon and titanium boride. The main objective of this study was to develop anode materials with high capacity and study the effect of milling on the electrochemical properties. In addition, microstructural and electrochemical analyses were used to identify the optimum experimental condition required for obtaining high capacity.

EXPERIMENTAL

Nanocomposites of silicon and TiB₂ were prepared using a SPEX-8000 high-energy mechanical mill. A hockey puck cell design was used employing lithium foil as an anode and 1 M LiPF₆ in EC/DMC (2:1) as the electrolyte. All the batteries tested in this study were cycled in the voltage range from 0.02–1.2 V employing a current density of 0.1 mA/cm² using an Arbin potentiostat. The phases present in the as-milled powders and the cycled electrode were analyzed using x-ray diffraction (Rigaku, Cu K α , θ/θ diffractometer), while the microstructure and chemical composition of the electrode was examined using a scanning electron microscope (Philips XL30, equipped with EDX).

RESULT AND DISCUSSION

Similar to the Si/TiN system, XRD analysis on the Si/TiB₂ composite indicates that Si also exists as an amorphous phase even after milling for 6 h. All the peaks in the patterns correspond to TiB₂ and the broad nature of the peaks are clearly indicative of the nanocrystalline nature of the boride. The reason for the presence of nanocrystalline-amorphous Si after milling is due to the high hardness of the matrix such as TiN and TiB₂ which play an important role in pulverizing Si into very fine amorphous particles.

The specific gravimetric and the equivalent volumetric capacity of the electrode prepared with these powders including 40 mol% Si are shown in Fig. 1. The overall capacity appears to decrease as the milling time is increased, indicating a reduction in the amount of the active silicon phase. However the sample milled for longer time shows better capacity retention. Although the reason for reduction in capacity with an increase in milling time is not clear yet, possible explanation for this is the embedding of Si or a decrease in its activity due to its reaction with the inactive matrix. The composite obtained after milling for 25 h exhibits a good stable capacity about 350 mAh/g.

In order to investigate the effect of initial size of TiB₂ on the electrochemical properties of anodes, pre-milled TiB₂ with different milling time have also been used to generate Si/TiB₂ nanocomposites. As seen in Fig. 2, 18h pre-milled sample shows better stability in terms of capacity retention without losing

much capacity known to occur from extended mechanical milling as shown in Fig 1. This result indicates that small particle size of inactive component provides better stability because the stress induced by volume expansion during cycling is distributed more homogeneously in the composite with pre-milled inactive components. This may be one of the preferred ways to improve the stability of active-inactive nanocomposite anodes.

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REFERENCES

1. Y. Idota, A. Matsufuji, Y. Maekawa, and T. Miyasaki, *Science*, **276**, 1395 (1997).
2. O. Mao and J. R. Dahn, *J. Electrochem. Soc.*, **146**, 423 (1999).
3. K. D. Kepler, J. T. Vaughey, and M. M. Thackeray, *Electrochem. Solid-State Lett.*, **2**, 307 (1999).
4. M. Winter and J. O. Besenhard, *Electrochim. Acta*, **45**, 31 (1999).
5. H. Kim, J. Choi, H. J. Sohn, and T. Kang, *J. Electrochem. Soc.*, **146**, 4401 (1999).
6. I. S. Kim, P. N. Kumta and G. E. Blongren, *Electrochem. Solid-State Lett.*, **3**, 493 (2000).

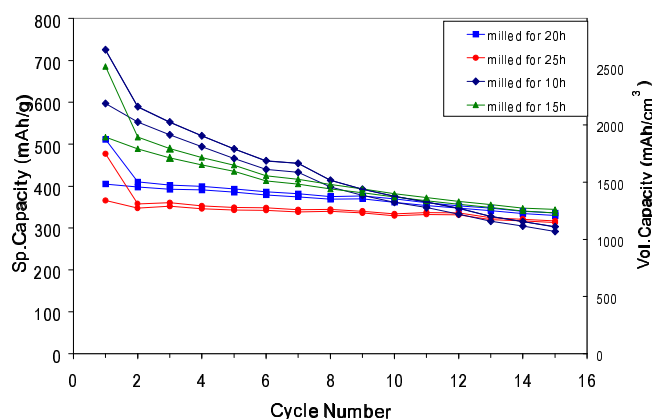


Fig. 1. Capacity as a function of cycle number for Si/TiB₂ nanocomposites containing 40 mol% Si obtained after milling for 10 h, 15 h, 20 h and 25 h each.

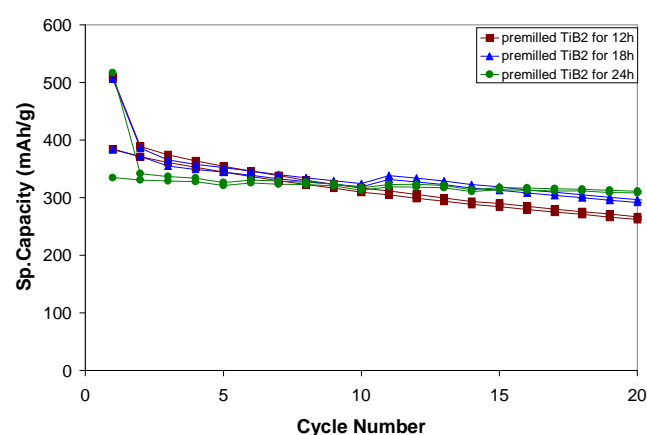


Fig. 2. Capacity as a function of cycle number for Si/TiB₂ nanocomposites containing 33 mol% Si obtained after milling with pre-milled TiB₂ for 12 h. The TiB₂ was pre-milled for 12 h, 18 h and 24 h.