SnSb anode in a SnSb/NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂ Na-ion battery

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Introduction

The practical application of sodium-ion batteries requires electrode material that will provide high-voltage and high-capacity leading to cells with high-energy density. In fact our energy density calculations have shown that Na-ion batteries can potentially reach as high as 220 Wh/kg.¹ However, even to reach the 150 Wh/kg threshold would require a cathode and anode that possess high-capacity of 180 and 500 mAh/g (with first cycle low irreversibility), respectively, with 3 V cell operation. Sodium electrochemically reacts at low voltage with SnSb² alloy anode and it has shown good high-capacity and cycling properties. This work examines both the SnSb anode and its use in a Na-ion battery.

Experimental

SnSb/C nanocomposites were prepared by high energy ball milling under an argon atmosphere. The SEM images showed the primary particle size was about 10-20 nanometers while the secondary particle aggregated to 1-3 micrometers. Layered NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂³ was synthesized and used as the cathode. Coin cells (2032) were cycled in 1M NaPF₆ solution in EC:EMC (3:7) with 5% FEC SEI additive was used as electrolyte. The current density was 10 mA/g based on the active cathode material. The relative anode:cathode ratio was approximately 1.4:1 based on the calculated capacity.

Results and Discussion

Apart from the first formation cycle, the SnSb/NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂ cell exhibits smooth monotonic voltage profiles that are shown in Fig. 1(a). The first cycle irreversible capacity loss is attributed to SEI formation and Na trapping in the carbon portion of the nanocomposite. The reversible cell capacity observed is 75mAh/g (cathode basis) at C/10 after 50 cycles with an average voltage of 3 V. This amounts to about 35% of the total Na cycled into and out of the layered cathode. The discharge capacity retention after 50 cycles is 92.5% and the coulombic efficiency is very close to 100% after the first cycle.

The SnSb/NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂ cell voltage profiles are indicative of two single phase intercalation reactions in both the anode and cathode. Fig. 2 is the *in situ* XRD patterns (synchrotron –X-rays) of Na/SnSb cell during the first cycle. As it is apparent, the SnSb which starts out crystalline immediately turns amorphous upon Na insertion; the material also fails to revert to its original SnSb alloy phase upon Na removal. Since the Na phases of SnSb formed are amorphous, they would likely buffer the volume change upon sodiation better than that of pure sodium alloy phases of Sn and Sb which would lead to improved cycleability. We will discuss the battery chemistry and the mechanism of sodium insertion into SnSb alloy in this presentation.

References

1. M. Slater, D. J. Lee, D. Kim and Christopher

Johnson, *Adv. Funct. Mater.*, 23, 947, (2013); K. Gallagher and P. Nelson, BatPaC 2013.

- L. Xiao, Y. Gao, J. Xiao, W. Wang, L. Kovarik, Z.Nie, J. Liu. *Chem. Commun.*, 48, 3321, (2012)
- D. Kim, E. Lee, M. Slater, W. Lu, S. Rood, C. Johnson *Electrochem. Comm.*, 18, 66, (2012)

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Figure 1: (a) Voltage profiles of SnSb/NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂ between 2-3.9V, from right to left 1st cycle, 5th cycle, 10th cycle, 20th and 50th cycle. (b) Cycling performance of SnSb/NaNi_{1/3}Mn_{1/3}Fe_{1/3}O₂ at a current rate 10mA/g based on the active cathode material



Figure 2. XRD patterns and corresponding voltage profile of the in situ Na/SnSb alloy anode cell.