

Short Communication

Electrochemical Properties of Si Negative Electrodes Bonded with Partially Hydrolyzed Polyacrylamide for Li-ion Batteries

Hong-Bin Qiao*, Xue-Mei Tian*, Ting-Feng Yi*

School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China

*E-mail: qiaohb@ahut.edu.cn (Hong-bin Qiao); tianxuemei_000@163.com (Xue-mei Tian); tfyihit@163.com (Ting-feng Yi)

Received: 7 May 2013 / Accepted: 12 June 2013 / Published: 1 July 2013

Si negative electrode bonded with partially hydrolyzed polyacrylamide (HPAM) was prepared, the performance of the charge/discharge cycle of lithium-ion batteries was studied, and the surface morphologies of the electrodes after the charge/discharge cycle was observed using the SEM. The coulombic efficiency of the Si-based electrode increased from less than 30% of initial cycle to over 90% after 50 cycles. SEM indicated that the HPAM binder was a much more effective restraint on volume expansion in active Si materials during the charging process. The discharge capacity of Si-HPAM electrodes was approximately 120% and 111% after 50 cycles, respectively, compared to the first cycle in the voltage range of 0.07-1.2V and 0.06-1.0V, which was attributed to the excellent maintenance of an electrical-conducting network during cycling and inhibiting the powders pull-off from the surface of the electrodes effectively. Few active powders detached from the surface after the charge/discharge test, as a result of the formation of the three dimensional network structure, which was benefit to the long service lifetime of the lithium-ion batteries.

Keywords: Si-based electrode; HPAM; Binder; Volume expansion; Lithium-ion batteries

1. INTRODUCTION

Silicon has attracted much attention due to the theoretical storage capacity for the $\text{Li}_{22}\text{Si}_5$ alloy is 4200mAhg^{-1} . However the insertion and extraction of lithium induce mechanical strain, which causes the cracking of Si particles and loss of electrical contacts between Si and the conducting agent, resulting in a loss of connectivity with the electrode which causes poor cyclability in practice [1-5]. An important approach to resolving the problem is the optimization of the chemical structure of polymeric binder in a Si negative electrode. The cycle life of Si negative electrodes was improved using a binder

containing the sodium carboxymethyl cellulose (NaCMC). The efficiency of NaCMC binder could be attributed to its extended conformation in solution that facilitates the formation of an efficient conductive material, binder and silicon components[1]. Both the NaCMC and the partially hydrolyzed polyacrylamide (HPAM) are widely used as thickener and in water treatment, paper making, petroleum, coals, textiles and construction etc[6, 7], and the latter may be the substitution for the former in the coating industry and in binding the conductive material of Si negative electrodes. The commercial Nafion solution was ion exchanged with LiOH, to create a flexible and Li-ion conductive binder, as the high proton and water content of Nafion may be problematic for Li-ion battery electrodes[8]. In this investigation, for the first time, the preparation and electrochemical performance of silicon with AB (Acetylene Black) negative electrodes using HPAM binder was studied.

2. EXPERIMENTAL

Preparation of silicon electrodes.—Si(99%, 325 mesh, Aldrich) was used as the active material and acetylene black (ERA CHEM) as the conductive agent in the negative electrodes. Partially hydrolyzed polyacrylamide (HPAM, MW 200000, KANTO CHEM) was used as binder and silane coupling agent (KBM-903, SHINETSU) was used to treat the particles in the slurry. Measured amounts of Si, AB, silane coupling agent (CA) and binder were added to a sealed bottle according to the electrode formulation of 60 wt % Si, 20 wt % AB, 0.1 wt % CA and 19.9 wt % binder. Additional amounts of pure water was added to give the mixture an appropriate viscosity. All the chemicals were used as received. A magnetic stirrer was used to mix the composites in the bottles at 600 rounds per min for over 10 hours in room temperature. LiOH (KANTO CHEM) was added in the suspension to neutralize carboxylic groups in HPAM. Then, the slurries were spread on a copper foil. The wet electrodes were heated at 107-110°C in vacuum overnight to remove the water.

Electrochemical characterization.—Silicon electrodes with HPAM binder were assembled using a lithium foil disk as a common counter and reference electrode. The electrolyte used was 1 M LiPF₆ (Stella, Japan) dissolved in a mixed solution of ethylene carbonate (EC) and propylene carbonate (PC) with volume ratio 1:1. The cells were assembled and crimped closed in an Ar-filled glove box.

The half cells were galvanostatically charged and discharged at a current density of 0.1C in the voltage range of 0.06-1.0V and 0.07-1.2V, respectively, vs Li/Li⁺ using battery test cycler (HJ-201B, Hokuto Denko). Cyclic voltammetry (CV) was conducted by scanning a Cu electrode in a conventional three-electrode cell from 0.02 to 1.2 V with the scanning rate 0.1 mV/s using 1 M LiPF₆/EC-PC (1:1 vol%) as electrolyte. The response was recorded on a computer-controlled potentiostat (HZ-5000, Hokutodenko), Li metal used as the counter electrode and the reference electrode.

Scanning electron microscopy.—High-resolution images of the silicon electrodes after the charge/discharge cycles were obtained with a JEDL JSM-6490LV scanning-electron microscope (SEM). Imaging was performed at 15 kV accelerating voltage.

Infrared spectroscopy. —The structure of the HPAM was characterized by Fourier transform infrared spectroscopy (FTIR) (Spectrum one, Perkin Elmer) in the range of $500\text{--}4000\text{cm}^{-1}$. The samples air-dried in a desiccator for a minimum of 24 h were pelleted with dried, spectroscopic grade, potassium bromide for FTIR analysis.

3. RESULTS AND DISCUSSION

Fig.1 shows the discharge capacity of HPAM samples during the charge/discharge cycle. As can be seen, the discharge capacity of the sample with the cut-off voltage 0.07-1.2 V is higher than that of the one with 0.06 to 1.0 V, and the first discharge capacity is 90 mAh/g and 72 mAh/g, respectively, then gradually increase with the cycle number, reaching the maximum circulation after 20 cycles, keep 150% and 138%, respectively, compared with the initial discharge capacity. The discharge capacity keep 120% (108 mAh/g) and 111% (80 mAh/g) respectively, showing excellent electrochemical properties after 50 charge/discharge cycles. The results show that both the active material and the conductive material in HPAM bonded silicon anode are activated at the beginning, and are inspired to better contact performances.

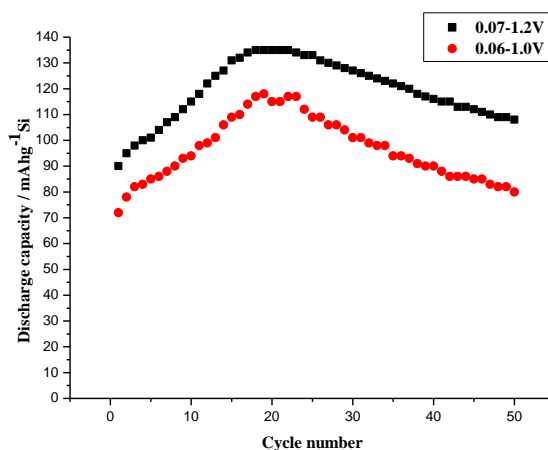


Figure 1. Discharge capacity of Si negative electrode bonded with HPAM

The coulomb efficiency of the first cycle at the charge/discharge cut-off voltage 0.07-1.2 V and 0.06-1.0V are 29% and 21%, respectively (in Fig.2), and of the second cycle, 73% and 69%, respectively, keeping steadily increasing with the cycle number. The reason of the low coulomb efficiency of the first cycle may be the existence of amorphous carbon dioxide layer and the pores on the surface of the silicon [9,10], besides the formation of the SEI film. Another possibility is, because of the limitation of experimental conditions, the presented oxygen-containing groups on acetylene black react with lithium ions, which cannot then deintercalate, causing the low coulomb efficiency, on the other hand the coulomb efficiency increased gradually with the stretching of HPAM in the process of charge/discharge. The coulomb efficiency reach over 85% after eight cycles and then gradually and

slowly increase to 50 cycles, forming a relatively stable deinsertion and insertion process of lithium ion. The coulomb efficiency reach as high as 92% and 91% after 50 cycles, showing the excellent circulation stability of the material.

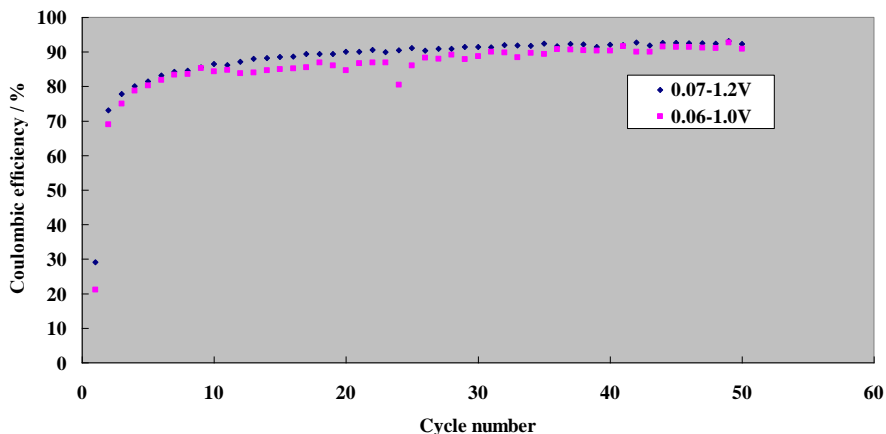


Figure 2. Coulombic efficiency of Si negative electrode bonded with HPAM

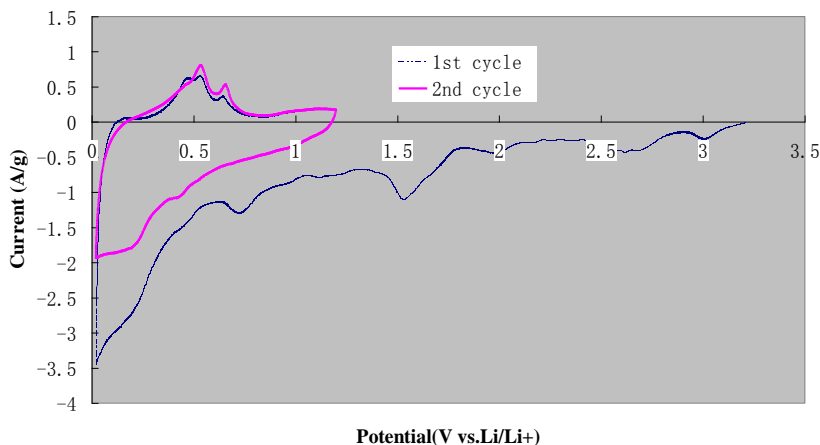


Figure 3. Cyclic voltammogram of Si negative electrode bonded with HPAM (scanning rate: 0.1 mV/s, Electrolyte: 1M LiPF₆/EC:P C(1:1 vol%))

Fig.3 shows the cyclic voltammogram (CV) of HPAM bonded AB/Si mixture (inset) during the first two charge–discharge cycles. The HPAM exhibits different anodic and cathodic performance in the first cycle compared to the following cycles. A anodic peak is measured near 1.55 V, and it is from the lithium intercalation into disordered carbon that contained in the HPAM. This process is irreversible because no corresponding cathodic peak at 1.55 V can be observed. There is a primary anodic peak below 0.75 V during the 1st cycle, and it should be contributed together by the lithium intercalation into the AB and silicon, and the formation of solid electrolyte interphase (SEI). It is widely acknowledged that lithium can insert into silicon below 0.4 V [11] and can deliver a capacity of more than 2000 mAh g⁻¹, so this anodic peak is considered from the lithium intercalation to HPAM and alloying with silicon nanoparticles. there are several plateaus corresponding to different lithium

insertion/extraction processes. The initial columbic efficiency is only 20%~30%. The irreversible capacity loss in the 1st cycle can be ascribed to the presences of the SiO₂ layer on the surface of silicon nanoparticles [12] and the micropores on the surface of disordered AB[13].

FTIR spectra of the HPAM material and the bonded sample are shown in Fig.4. There is a peak at 617 cm⁻¹, which is attributed to the bending vibration of the NH₂ group. Peaks at 1121cm⁻¹ shifting and merging to 1115cm⁻¹ are attributed to the formation of Si–O–Si bond. The vibration peak at 1655cm⁻¹ and 3430cm⁻¹ of the H-O-H bond indicate the existence of the capillary water and bounded water on the material surface, as a result the electrode cyclic performance is affected to some extent. So the dehydration process need to be further improved.

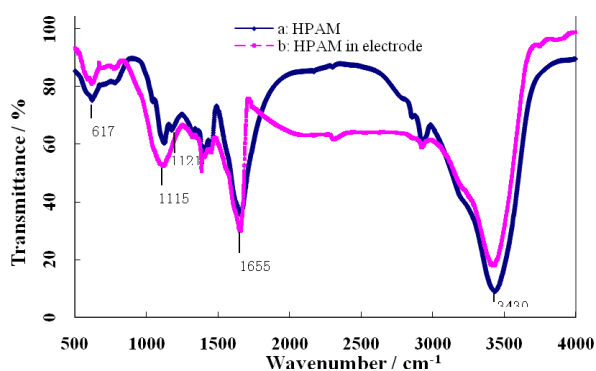
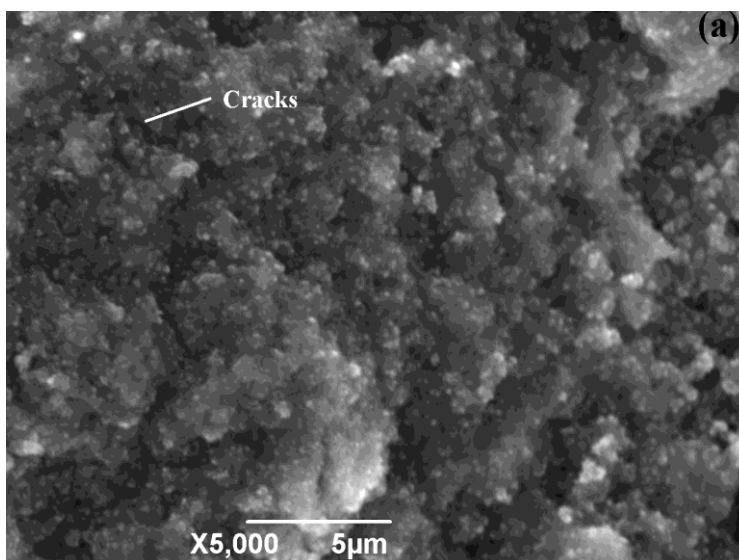


Figure 4. FTIR spectra of the HPAM and Si negative electrode with the HPAM binder

Fig. 5 shows the scanning electron microscopy (SEM) of the silicon anode bonded with HPAM after 50 charge/discharge cycles. Round shape, uniform particles with the average diameter 300 nm can be found on the material surface.



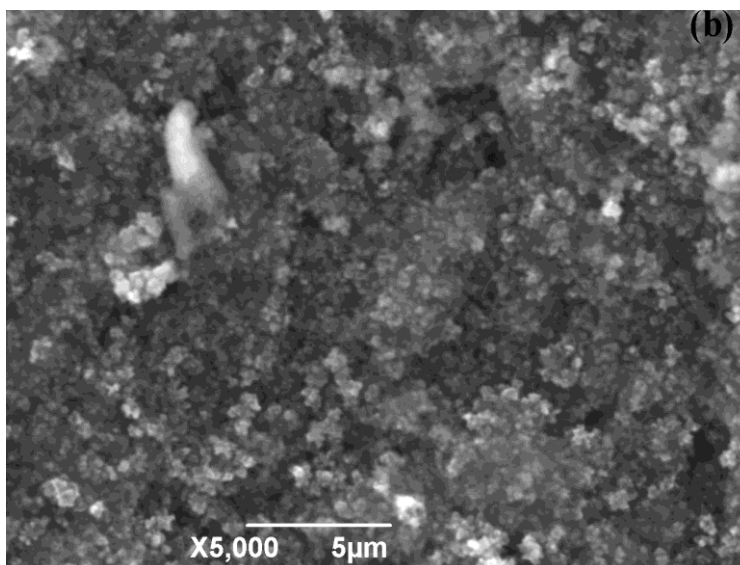


Figure 5. SEM images of Si negative electrode bonded with HPAM after 50 cycles (a:0.06-1.0V, b:0.07-1.2V)

No collapse of structures caused by the volume change are found. The smaller particles and good dispersity is mainly associated with the molecular chain flexibility of HPAM, which is beneficial to the formation of a dense layer of three dimensional network structure, restraining the expansion of the plate during the charge/discharge cycle effectively, reducing the loss of active material and improving the cyclic lifetime of the electrode. From Fig.5 (a), certain cracks occurs on the plate surface after the cycle, may affect the circulation performance to a certain extent, while Fig.5 (b) shows more uniform plate surface, indicating the higher coulomb efficiency and discharge capacity than the former.

4. CONCLUSIONS

HPAM was successfully used as a binder of Si negative electrodes, and the electrochemical reversibility of active Si material was improved by using HPAM binder during cycling. The electrochemical reactivity of HPAM binder in negative electrodes was clearly elucidated by FT-IR analysis. Although HPAM binder reacted with Li ions and electrons during the first charge process, the cyclic degradation of active Si material could be remarkably reduced by using HPAM binder with high tensile strength. Due to the poor electrical-conducting network in Si-HPAM after Li⁺ insertion, Li ions were hardly extracted from active Si material during Li⁺ extraction, and the discharge capacity rapidly declined. These results show that a robust polymeric binder like HPAM can enhance the electrochemical properties of Si negative electrodes, causing large dimensional changes during cycling. The results of the experiments indicate that more work is needed in order to improve charge/discharge properties of the half cell in minimizing the size of the Si particles and improving the process of preparing the electrodes.

ACKNOWLEDGEMENTS

Prof. Jing Zhu in our laboratory is gratefully acknowledged for carrying out the FT-IR analysis. This work was financially supported by the Key project of Scientific Research Foundation sponsored by Education Department of Anhui Province, China (no. KJ2013Z016), the teaching research project (no. 2011jg59) and the Program for Innovative Research Team (no. TD201202) in Anhui University of Technology.

References

1. H. S. Kim, K. Y. Chung, B.W. Cho, *J. Power Sources* 189 (2009) 108.
2. X.-y. Zhou, J.-j. Tang, J. Yang, Y.-l. Zou, S.-c. Wang, J. Xie, L.-l. Ma, *Electrochim. Acta* 70 (2012) 296.
3. H.Y. Lee, S.M. Lee, *J. Power Sources* 112 (2002) 649.
4. N. Dimov, S. Kugino, M. Yoshio, *J. Power Sources* 136 (2004) 108.
5. X.-y. Zhou, J.-j. Tang, J. Yang, J. Xie, L.-l. Ma, *Electrochim. Acta* 87 (2013) 663.
6. T. H. Park, J. S. Yeo, Y. Ohata, M. H. Seo, J. Miyawaki, I. Mochida, S. H. Yoon. *Int. J. Electrochem. Sci.* 8 (2013) 249.
7. M. Bjørsvik, H. Høiland, A. Skauge. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 317(2008) 504.
8. R. R. Garsuch, D Le, A Garsuch, J. Li, S. Wang, M. Farooq, J. R. Dahna, *J. Electrochem. Soc.* , 155(2008)721.
9. J. Saint, M. Morcrette, D. Larcher, *Adv. Funct. Mater.* 17 (2007)1765.
10. Y. Wu, C. Wan, C. Jiang, *Carbon*, 37 (1999) 1901.
11. H. Li, X.J. Huang, L.Q. Chen, Z.G. Wu, Y. Liang, *Electrochem. Solid-State Lett.* 2 (1999) 547.
12. J. Saint, M. Morcrette, D. Larcher, L. Laffont, S. Beattie, J.P. Peres, D. Talaga, M. Couzi , J.M. Tarascon, *Adv. Funct. Mater.* 17 (2007)1765.
13. Y.P. Wu, C.R. Wan, C.Y. Jiang, S.B. Fang and Y.Y. Jiang, *Carbon* 37 (1999) 1901.