The SiC/SiO Nanostructured Core-Shell as Anode Material for Lithium Ion Batteries: Synthesis and HRTEM Characterization

P. Moradifar*, B. Bahman-Nezhad, M. Abdorahim, S. Darvish, S. Asgari

Material Science and Engineering Department, Sharif University of Technology, Tehran, Iran

The SiC/SiO nanocmposite was synthesized by a sol-gel method with a following heat-treatment process. The SiC nanoparticles were coated with SiO, as a result, a core-shell nanostructured was formed. The processed material was characterized using X-ray energy dispersive spectroscopy (XEDS), high resolution transmission electron microscopy(HRTEM), fourier-transform IR spectroscopy (FTIR). Data obtained in this research showed that core-shell nanoparticles of SiC/SiO with an average range size of 20-40 (nm) may be produced through sol-gel processing. The SiC/SiO core-shell nanocomposite can act as regarded candidate for high performance anode materials for lithium ion battery applications.

Keywords: Lithium ion battery, Core-shell; SiC/SiO Nanocomposite, Sol-gel.

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1. INTRODUCTION

In recent years, electronic devices have been significantly improved in terms of power efficiency and memory capacity [1]. Since Lithium-ion batteries that have been mainly used for portable electronic devices are now extensively being used in applications such as power tools and hybrid electric vehicles (HEVs), plug-in-hybrid electric vehicles (PHEVs) and other electric utilities [2], commercial graphite anode can not satisfy the increasing demand for higher capacities. Therefore, finding new electrode materials with higher capacities or higher energy densities has been one of the main routes in recent research activities. Silicon and silicon-based materials have been regarded as potential candidates for anode applications in rechargeable lithium-ion batteries [3]. This is mainly due to their high charge capacity with a theoretical capacity of 4200 (mAhg^{-1}) for the fully lithiated composition Li$_{4.4}$Si. This is significantly better than that of the commercially used graphite (372mAhg^{-1}) together with better safety features and non-memory effect resulting from the relatively high lithiation potential [4]. These properties make silicon particularly attractive for potential large scale energy storage applications and various portable fields. There is one major problem with the application of Si as an anode, however, that is the large volume changes in silicon during charge-discharge cycles. This inevitably leads to pulverization of electrode and consequently a loss of inter-particle electronic contact of the electrode and an abrupt capacity fade after a few charge/discharge cycles [5,6]. There have been many investigations to overcome the large volume expansion of silicon anode materials by the preparation of nano sized Si [7,8], Si-based thin film [9], and Si-based composite anodes [10]. The performance of Si anodes can be significantly enhanced by the preparation of nanostructured electrode; since, the mechanisms of fracture will be changed when the material crystals are in a size of tens of nanometers scale. Another issue is related to the preparation

methods for silicon anode materials with high performance.to achieve a better cycling performance, this work reports a process which paves the way to prepare high performance anode material for li-ion batteries. Our approach was to create a nano-composite structure in which nano-sized particles are homogenously dispersed in an active matrix [11]. In this study we have tried to synthesis A SiC/SiO core-shell structure in which SiC nanoparticles(core) are encapsulated within SiO microspheres (shell) through sol-gel method and a following heat-treatment. The coated SiO can perform as a barrier to prevent the aggregation of the SiC nanoparticles. Simultaneously, the SiO shell can form lithium silicates, which serve as a buffer to reduce volume expansion of the SiC nanoparticles and consequently hinder abrupt capacity fade that occur after a few charge/discharge cycles. Furthermore SiO shell itself is an active material for additional Li-ion storage. Also, sol-gel process can provide several advantages in the fabrication of non-metallic and inorganic solid materials, considerably low working temperatures and facile production of porous films and bulk materials with various shapes in comparison with the several techniques such as flame or plasma-induced decomposition method.

2. RESULTS AND DISCUSSION

2.1 FTIR spectroscopy

Fig. 1 presents the FTIR spectrum obtained from the final nanopowder of SiC/SiO which confirms formation of Si-O and O-H bonds corresponding to different structural units of the network. The broad peakcentered at around 3470-3400 (cm^{-1}) is consistent with the overlapping of O-H bond of water molecules and SiO-H bond of surface silyl alcohol (silanol) molecules [12]. These silanol groups cause the adsorption of water molecules on the surface of materials. Furthermore, when the Si-O covalent bonds vibration occurs in the range of 1200-800 (cm^{-1}) itshows the existence of silica network (Si-O-Si) [13].

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* moradifar2000@dena.sharif.ir

As seen in Figure 1, an intense broad peak of Si-O appears at around 1100 (cm^{-1}) indicating that the molecules of SiO was formed during the sol-gel process.
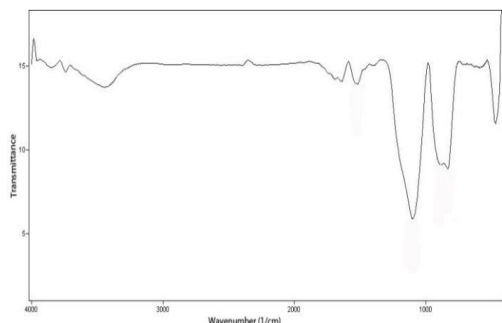

Fig. 1 – The FTIR spectra of the SiC/SiO core-shell

2.2 TEM Studies and Microanalysis

Fig. 2 shows a typical bright field image of the SiC/SiO core-shell. It reveals that the particle size of SiC with spherical morphology is in the range of 20-40 (nm). Also, the shell layers around particles are visible in the figure. In order to characterize the core-shell structure which was formed during the sol-gel process more precisely, HREM technique was employed. Figs. 3 and 4 show two micrographs obtained from the same sample. Fig. 3 shows the crystalline SiC core particles which are surrounded by an amorphous SiO shell layer, both have been proved in the next paragraphs. It is desirable that is silica formed with amorphous structure during the sol-gel process. This leads to the formation of highly branched clusters of silica interconnected after gelation and produces a random distribution of silica molecules as the shell layer on the surface of SiC core.
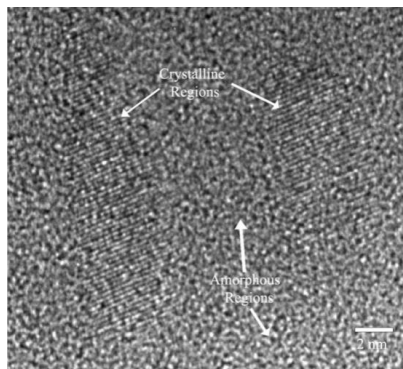

Fig. 2 – The HRTEM image of the SiC/SiO core-shell particles

Fig. 4 represents another HREM image of the SiC core particles taken from [110] zone axis. Using this figure, the value of interplanar spacing for (111) plane was measured to be 0.25 (nm). The measurements 0.25 (nm) and 0.21 (nm) correspond to the d-spacing of SiC {111} and {002} planes, respectively (SiC structure is cubic with the lattice parameter of 4.3589 angstrom). Moreover, the intersection angle between SiC {111} planes and the angle between SiC {111} and {002} planes are respectively 70 and 54 degree which are implied in Fig. 4. These values are in agreement with the crystallographic data for SiC material.
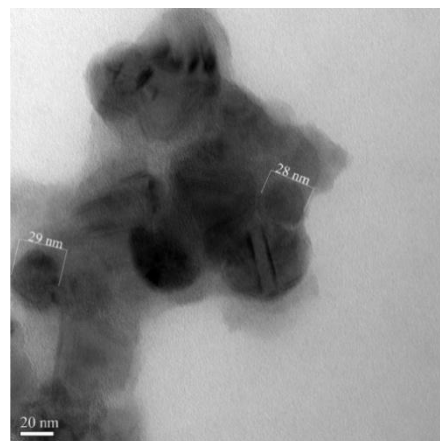

Fig. 3 – The magnified HRTEM image of the SiC/SiO core-shell showing the amorphous and crystalline regions
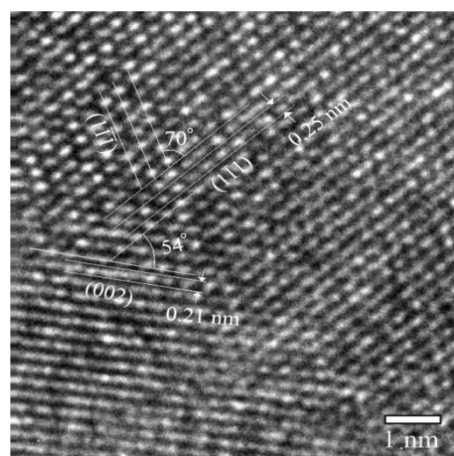

Fig. 4 – The magnified HRTEM image of the core region of the SiC/SiO core-shell

Fig. 5 shows microanalysis spectrum obtained from X-ray energy dispersive spectroscopy (XEDS) in point mode from an area marked by A in Fig. 3. This spectrum shows the presence of both Si K$_\alpha$ (1.74 KeV) as well as O K$_\alpha$ (0.523 KeV) peaks compatible with the shell composition of SiO$_2$. Besides, C K$_\alpha$ (0.282 KeV) and Cu L$_\alpha$ (0.928 KeV) peaks are clearly seen in this spectrum. The Cu peaks comes from the copper grid while the carbon peak is attributed to carbon support film and to a lesser extent to the SiC core.
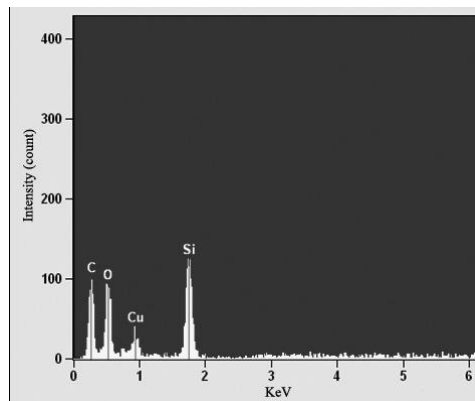

Fig. 5 – The XEDS spectra of the shell region of SiC/SiO core-shell

3. CONCLUSION

The core-shell SiC/SiO nanocomposite was synthesized by a sol-gel method followed heat-treatment by process. TEM studies reveals that the particle size of SiC with spherical morphology is in the range of 20-40 (nm), besides the FTIR spectrum can confirms thatmolecules of SiO was formed during the sol-gel process. The coated SiO can perform as a barrier to prevent the aggregation of the SiC nanoparticles. Simultaneously, the SiO shell can form lithium silicates, which serve as a buffer to reduce volume expansion of the SiC nanoparticles and consequently abrupt capacity fade after a few charge/discharge cycles. The processed nanocomposite can show better reversibility of lithium insertion/extraction and higher efficiency than SiC nanoparticles. The results of this investigation indicate that nanosized core-shell particles produced through sol-gel processing which can be employed to improve the electrochemical performance of Li-ion batteries.

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