

Preparation of SiO₂/Cu composites via modified Stöber and microwave-assisted methods

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Silica/copper (SiO₂/Cu) composites were prepared in nano-dimensions for use as anode materials in lithium-ion batteries. Modified Stöber and microwave-assisted methods were used to prepare of SiO₂ and Cu, respectively. The composites were prepared with different tetraethyl orthosilicate (TEOS) concentrations and mole ratios of TEOS to Cu²⁺ reactants. Cu was observed as the main phase in the products, which agglomerated into large particles, with some of them dispersed on the SiO₂ particles. SiO₂ appeared in the composites was amorphous phase and spherical in shape. Decreasing the TEOS concentration decreased the size of the SiO₂.

Key words: Silica, Copper, Nanocomposites and Lithium-ion battery.

Introduction

Secondary lithium-ion batteries are popular energy storages devices in portable electronics, due to their high energy density, no memory effect, long cycle life and long shelf life. Improving the technology is of considerable value, given the wide range of potential uses.

Anode material research seek to enhance both the energy density and mechanical stability of anodic electrodes [1-2]. Suggested improvements include alternating anode materials from graphite to higher theoretical specific capacity materials. Silicon is the most attractive element because of its high theoretical capacity (4200 mAh/g). However, it encounters with the large volume change (420%) during cycling [3]. Moreover, the silicon preparation is expensive, as it requires a multi-step and advanced fabrication process.

SiO₂, an oxide, has a lower theoretical specific capacity (1965 mAh/g) [4], but comparatively low volume expansion [5], and as a result has attracted interest as an alternative anode active component [4-7]. In addition, as one of the most abundant materials on Earth, it is inexpensive.

In this work, the nanostructure of SiO₂ was prepared to increase the charge rate from the short diffusion length of Li⁺ and increase the capacity from the large surface area of the small SiO₂ size. However, Si oxides have low electrical conductivity. As a result, this

research prepared SiO₂ composites with copper (Cu), a good electrical conductor. Small-sized of Cu was dispersed on the nano-spherical amorphous surface SiO₂ to serve as anode materials for lithium-ion batteries. The modified Stöber [8] and microwave-assisted methods were selected to prepare SiO₂ and Cu, respectively. These techniques offer one-step synthesis, use only simple reagents and equipment, can be carried out under normal atmospheric conditions, yield well-dispersed nanoparticles, are very low cost and are suitable for mass production. We believe that the composite of amorphous SiO₂ and conductive Cu can provide a high specific capacity with low volume change, providing a reasonable alternative anode material.

Experimental Procedure

Tetraethyl orthosilicate (TEOS, SIGMA-ALDRICH, 99.0%), 95% ethanol (Bangkok Alcohol Industries, 95%) and deionized (DI) water were mixed together. Formation of SiO₂ was initiated by adding 40% dimethylamine (DMA, M & B, 40%) solution under continual stirring for 1 hour. The final TEOS concentration was varied as 0.033, 0.026, 0.020, 0.013 and 0.007 M, while DMA and water concentrations were fixed at 0.40 and 11 M, respectively. The mixture was centrifuged and washed with ethanol to obtain SiO₂ particles. Next, the particles were added into the solution of Cu(NO₃)₂ · 3H₂O (CARLO ERBA, 99.5%) in ethylene glycol (J.T. Baker, 99.9%). In each condition, the mole ratios of TEOS to Cu(NO₃)₂ · 3H₂O were varied as 1 : 45, 25 : 25 and 30 : 25. Cyclical heating with a microwave oven (50 seconds, stop 3 minutes for 8 cycles) prepared the final products. The precipitate

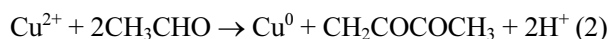
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from the solution was collected by centrifugation, washed with ethanol and dried at 60 °C in an oven.

The crystallinity and phase of the powders were obtained by using a powder X-ray diffraction (XRD, Rigaku Mini Flex II) technique. The morphology, size and elemental composition of all samples were analyzed by transmission electron microscopy (TEM, JEOL JEM-2010) and scanning electron microscopy (SEM, JEOL JSM-633SF) equipped with energy dispersive spectroscopy (EDS, JEOL JSM-5910FE).

Results and Discussion

X-ray diffraction patterns of the products are shown in Fig. 1. The face-centered cubic Cu (JCPDS 4-836) existed as a major phase in all products. Ethylene glycol decomposed to acetaldehyde and H₂O [9], followed by reduction of Cu²⁺ to Cu⁰, when the solution temperature was raised to about 170 °C due to microwave heating, as illustrated in equations (1) and (2).



The XRD pattern of the a-1 and b-1 samples, which were prepared by using 33 and 26 mM TEOS (1 TEOS: 45 Cu²⁺), respectively, showed that Cu₂O (JCPDS 77-199) occurred in the samples. The presence of Cu₂O was created by the stabilization of Cu¹⁺ by the

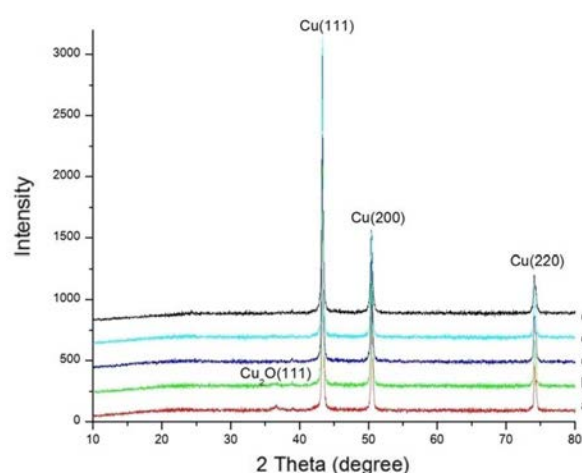


Fig. 1. The XRD patterns of the composites using TEOS concentrations of 33 (a-1), 26 (b-1), 20 (c-1), 13 (d-1) and 7 (e-1) mM and a TEOS: Cu²⁺ ratio of 1 : 45 mol.

appropriate reducing agent existing in the system [10]. In the procedure, the reducing agent was acetaldehyde, which was produced by the decomposition of ethylene glycol. Therefore, the Cu¹⁺ was present in the system in the form of Cu₂O in some of the products. Moreover, the Gibbs free energy change (G^0) of Cu₂O formation is more negative than G^0 of CuO formation [11], favoring the oxidation of Cu to Cu₂O over CuO. Therefore, the Cu₂O phase occurred with Cu in the products. For other products that their XRD patterns are shown in Fig. 1, the Cu₂O phase was not observed.

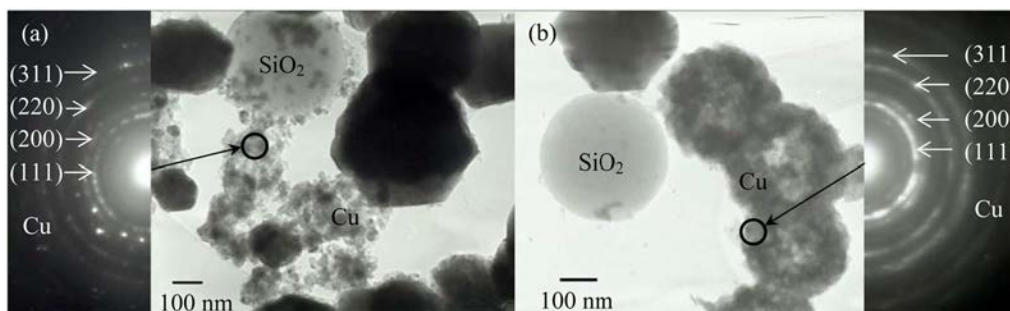


Fig. 2. The TEM images with SAD patterns of the samples using TEOS concentrations of 33 (a) and 26 mM (b). The TEOS: Cu²⁺ ratio was 1 : 45 mol.

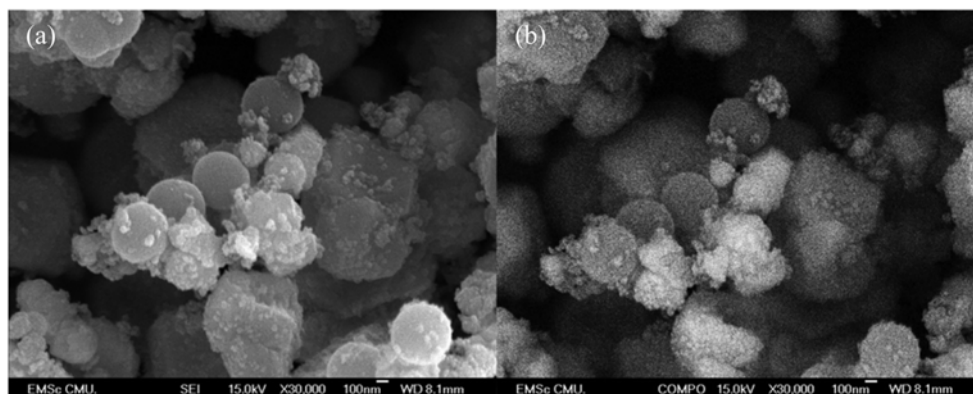


Fig. 3. The SEM image (a) and BEC image (b) of the sample using a TEOS concentration of 26 mM. The TEOS: Cu²⁺ ratio was 1 : 45 mol.

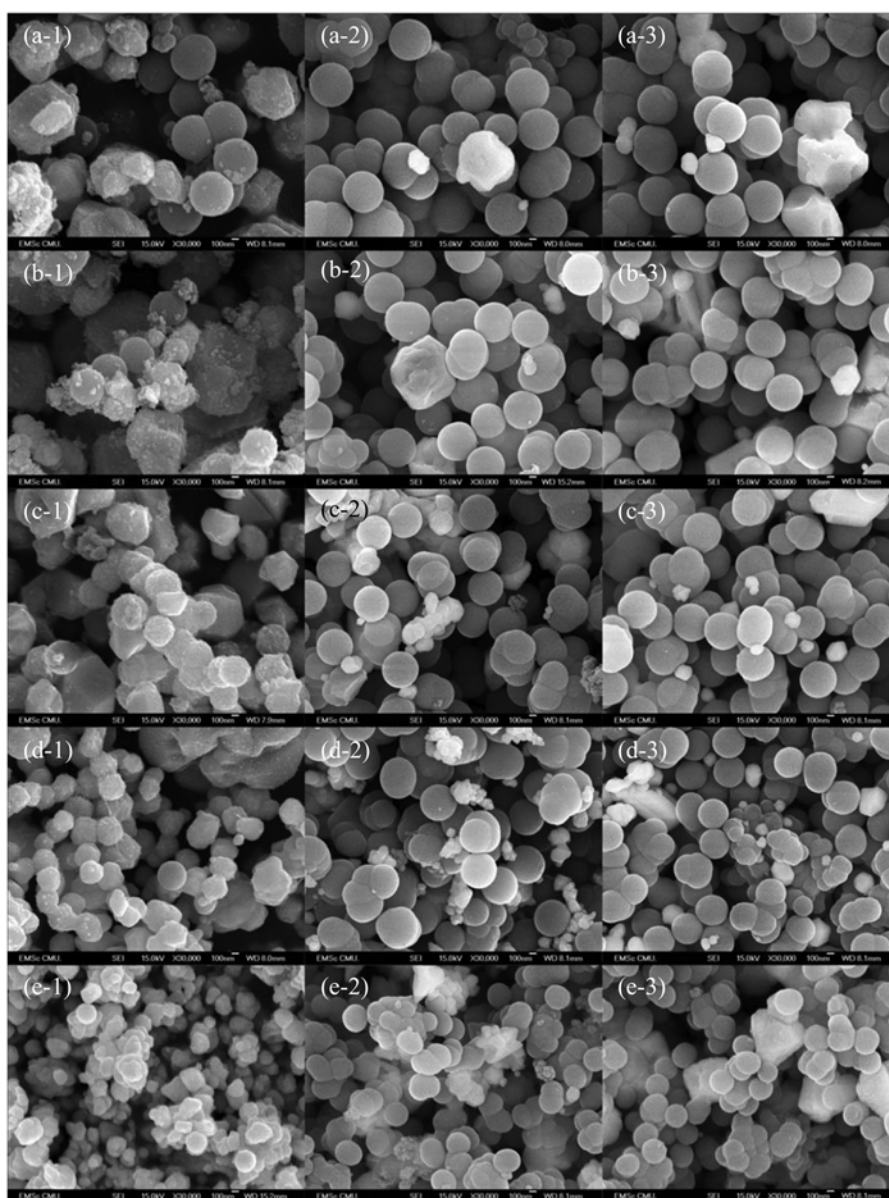


Fig. 4. High magnification SEM images of the prepared SiO_2/Cu composites using TEOS concentrations of 33 (a), 26 (b), 20 (c), 13 (d) and 7 mM (e). The notation (–1), (–2) and (–3) represent the mol ratios of TEOS: Cu^{2+} of 1 : 45, 25 : 25 and 30 : 25 mol, respectively.

The SiO_2 phase was not observed in the XRD patterns. This was because amorphous phase and low quantity of SiO_2 in the samples produced very low intensity, broad peaks that appeared as the part of the base line in the patterns.

The TEM images in Fig. 2 show that each product contained two different physical appearances. There are translucent amorphous SiO_2 sphere and opaque polygon Cu. The morphology and the composition of the other powder products are the same as two products as shown in Fig. 2.

Fig. 3(b) shows the backscattered electron contrast (BEC) image of the sample prepared by using 26 mM TEOS at 1 : 45 mol of TEOS : Cu^{2+} . The very bright areas in the BEC image present the various sizes of Cu. The rough bright areas on the globular SiO_2 surface

could indicate that some of Cu dispersed on the SiO_2 particles.

The SEM images in Fig. 4 show that the products were similar in morphology. They contained nano-spherical SiO_2 and non-spherical shaped Cu particles. The result from EDS (Table 1) corresponded to the XRD pattern that Cu existed as the main phase in the prepared composites. The increase in the mole ratio of TEOS to Cu^{2+} lead to an increasing percentage of O and Si by weight in the composites, as shown in Table 1. The increase of O and Si was possibly caused by an increase of SiO_2 in the composites; thus, the composites were composed of more spherical SiO_2 when the TEOS to Cu^{2+} mol ratios were increased.

Fig. 4 shows the SiO_2 particle size increased with increasing TEOS concentration (while water and DMA

Table 1. Elemental measurement by EDS technique for SiO₂/Cu composites (experimental conditions: 7 mM TEOS and TEOS: Cu²⁺ varied as 1 : 45, 25 : 25 and 30 : 25 mol).

Products	[TEOS] (mM)	TEOS : Cu ²⁺ ratio (mol)	% Weight of Element		
			O	Si	Cu
e-1	7	01 : 45	2.46	0.71	96.83
e-2	7	25 : 25	32.53	24.35	43.13
e-3	7	30 : 25	38.56	27.74	33.70

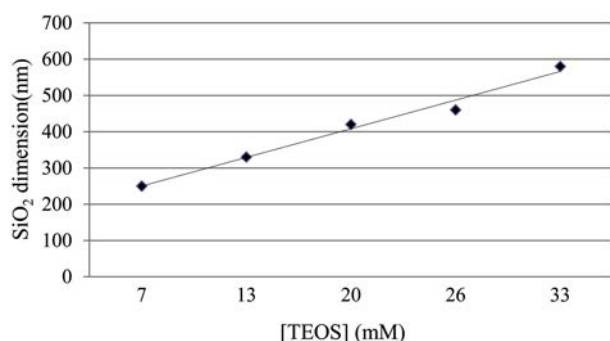
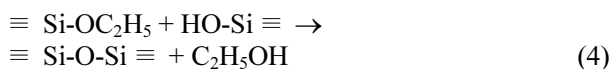
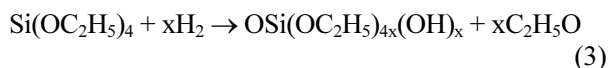


Fig. 5. Relationship of TEOS concentrations to SiO₂ particle dimensions.

concentrations were fixed). The SiO₂ diameters were 580, 460, 420, 330 and 250 nm when TEOS concentrations were 33, 26, 20, 13 and 7 mM, respectively. The relationship between SiO₂ particle size and TEOS concentration is illustrated in Fig. 5. In the Stöber process, SiO₂ particles are formed via the hydrolysis and condensation reactions, as expressed in equations (3) and (4), respectively [12]. The spherical SiO₂ particles were formed by self-aggregation of the nuclei from the condensation reaction. When the TEOS concentration decreased, the rate of hydrolysis and condensation slowed and the time available for forming nuclei lengthened. Consequently, a large number of total nuclei formed and the SiO₂ particle size was relatively smaller.



Finally, the small size and high percentage of SiO₂ in the composite is assumed to enhance the capacity of the anode material. As a result, the product prepared

from 0.007 mM TEOS using TEOS:Cu²⁺ of 30 : 25 offers potential as a suitable SiO₂/Cu nano-composite to use as anode material in lithium-ion batteries.

Conclusions

Crystal Cu particles occurred in all prepared SiO₂/Cu composites as the main phase with different morphologies-large opaque polygons and small particles of Cu, with some of them dispersed on the sphere SiO₂ particles. Some products contained Cu₂O, due to the stability of Cu¹⁺ in the acetaldehyde reducing agent and G⁰ favoring Cu₂O formation.

In all products, spherical SiO₂ occurred as amorphous phase. Decreasing the TEOS concentration yielded smaller SiO₂ sizes.

Acknowledgments

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References

1. D. Linden and T.B. Reddy, in "HANDBOOK OF BATTERIES" (McGraw-Hill, 2002) p. 35.16.
2. K. E. Aifantis, S. A. Hackney and R. V. Kumar, in "High Energy Density Lithium Batteries" (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010) p. 129-130.
3. H. Wu and Y. Cui, Nano Today 7 (2012) 414-429.
4. N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu and Q. Chen, Sci. Rep. 3 (2013).
5. M. Sasidharan, D. Liu, N. Gunawardhana, M. Yoshio and K. Nakashima, J. Mater. Chem. 21 (2011) 13881-13888.
6. B. Guo, J. Shu, Z. Wang, H. Yang, L. Shi, Y. Liu and L. Chen, Electrochem. Commun. 10 (2008) 1876-1878.
7. H. Guo, R. Mao, X. Yang and J. Chen, Electrochim Acta 74 (2012) 271-274.
8. Y. Kobayashi, H. Katakami, E. Mine, D. Nagao, M. Konno and L.M. J. Liz-Marzán, J. Colloid Interface Sci. 283 (2004) 392-396.
9. L. Gou, M. Chipara and J.M. Zaleski, Chem. Mater. 19 (2007) 1755-1760.
10. Y. Zeraatkish, Y. Ghayeb, E. Keshavarzi and K. Karami, Middle East J. Sci. Res. 8 (2011) 92-94.
11. N. Furushiro, M. Higuchi, T. Yamaguchi, S. Shimada and K. Obata, Precis. Eng. 33 (2009) 486-491.
12. I.A.M. Ibrahim, A.A.F. Zikny and M.A. Sharaf, J. Am. Sci. 6 (2010) 985-989.