International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

SiO₂@graphite Composite Generated from Sewage Sludge as Anode Material for Lithium Ion Batteries

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Received: 15 July 2017 / Accepted: 6 September 2017 / Published: 12 October 2017

Sewage sludge treatment is an annoying issue due to the environmental pollution. We herein demonstrate the effective conversion of sewage sludge to a potential anode material for lithium ion batteries (LIBs) by a simple annealing method combined mechanical milling. The generated silica (SiO₂) hybridized with a handful of graphite exhibits good electrochemical performance. Stable reversible capacity of 433 mAh g⁻¹ is achieved after 100 cycles at 100 mA g⁻¹. At a high current density of 1000 mA g⁻¹, the reversible capacity is still stabilizing at 244 mAh g⁻¹ after 500 cycles, demonstrating the waste sewage sludge is a potential LIBs anode source.

Keywords: SiO₂; Graphite; Sewage sludge; Lithium ion batteries; Anode materials

1. INTRODUCTION

Lithium ion batteries (LIBs) are still in the ascendant for applications to portable electronics, electric vehicles (EVs) and hybrid EVs in the past decades [1-3]. In the case of anode materials for LIBs, although various alternative candidates have been constantly emerging, such as alloys, metal oxides, metal sulfide, and carbon hybrids, graphite-based anodes still dominated the market of commercialized anode materials [4-6]. However, graphite mine is a non-renewable resource, meaning that exploitation and utilization of graphite is not limitless so far.

Silica (SiO_2) is almost an unlimited resource on Earth, which exists widely in soils and sands and so on [7, 8]. Apart from its natural occurrence, SiO_2 is also present in many materials such as waste glasses, beverage or food containers, and sewage sludge [9]. Some part of these waste materials are recycled and reused, but majority of them are discarded into the environment, especially sewage sludge, thus inevitably causing the environmental pollution. By making use of the sewage sludge, SiO_2 can be generated sustainably for use as potential energy storage material. The initial investigations indicate that SiO_2 was electrochemically inactive when applied as LIBs anodes until Gao et al. reported that nano-SiO₂ could reversibly react with lithium at low potentials [10]. After that, many researches on nano-SiO₂ with various structures have been reported for applications as LIBs anodes, such as thin film, nanotube, hollow nanocube or nanosphere, carbon-coated nanoparticles and so on [8, 11-19]. However, the reported processes generally required complex procedures with employing high cost precursors.

To the best of our knowledge, utilizing sewage sludge as a precursor for LIBs anode materials has never been reported in the literatures. We herein demonstrate the effective conversion of sewage sludge to a potential anode source for LIBs by a simple annealing method combined mechanical milling. The successful recycle of sewage sludge not only reduces the immoderate consumption of graphite, but also offers a valuable clue for cost-effective and ecologically acceptable sludge treatment.

2. EXPERIMENTAL

The raw sewage sludge was collected in Xi'an city (Shaanxi, P. R. China). Before annealing, the sewage sludge was dried at 110 °C for 2 h. Then the pretreated sewage sludge was annealed at 600 °C for 4 h under the argon atmosphere. After being cooled to room temperature naturally, the solid product was collected and mixed with graphite powder (Sinopharm Chemical Reagent Co.) with different weight ratios (16:1, 16:2, 16:3). The mixture were milled using a planetary mill (QM-3SP2, China) with a ball-to-powder weight ratio of 25:1 at 400 rpm for 20 h. To avoid the increase in temperature during milling process, the milling treatment was interrupted every 2 h and rested for 1 h. The as-obtained products were denoted as S1, S2, and S3, corresponding to the above mentioned weight ratios. For comparison, the sample without graphite was also prepared under the same condition, and was denoted as S0.

X-ray powder diffraction (XRD) patterns were carried out on a Rigaku D/MAX2200PC diffractometer with Cu K α radiation. Scanning electron microscopy (SEM) images were acquired on S-4800 SEM (Hitachi, Japan). The detailed structures of products were characterized with transmission electron microscopy (TEM, FEI, F20G)) and high resolution TEM (HRTEM, FEI, F20G) equipped with selected area electron diffraction (SAED) and an energy-dispersive X-ray spectroscopy. Raman spectroscopy was measured on a Renishaw RM 1000 spectromicroscopy system using the 532 nm Ar laser.

The electrochemical measurements were conducted on 2032 coin cells using the as-prepared samples as anodes (the working electrode). The working electrode was prepared by mixing the active materials, acetylene black, and polyvinylidene fluoride (PVDF) (in N-methyl-2-pyrrolidone) with a weight ratio of 80 : 10 : 10. The obtained slurry was coated onto a copper foil and dried at 120 °C for 10 h under vacuum. The foil was finally cut into circle discs with a diameter of 16 mm as the anode in the 2032 coin cells. Besides, the pure Li foil was utilized as a counter electrode, Celgard 2500

membrane as separator, and 1.0 mol L^{-1} LiPF₆ in mixture EC and DMC (1 : 1 in volume) as electrolyte. All the coin cells were assembled in an argon-filled glove box. The charge-discharge tests were performed on a Newaresles battery test system (BTS) (Shenzhen, China) in a voltage range of 0.01-3.0 V at different current rates. The capacity was calculated based on the mass of active material. Cyclic voltammetry (CV) was carried out at room temperature on an electrochemical workstation (CHI 660E). Electrochemical impedance spectral measurements were carried out in the frequency range from 100 kHz to 0.01 Hz on a CHI 660E electrochemical workstation.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the powder samples. The main peaks centered at 21° , 26° , and 50° of the samples are indexed to crystal planes (100), (101), and (112) of hexagonal SiO₂ (JCPDS NO: 46-1045), indicating that the major solid constituent of sewage sludge after annealing is SiO₂. The peak of graphite in the milled composites is probably overlapped by the main peak of SiO₂ at 26° [20-22]. However, the relatively reduced intensity of the peak at 26° indicates the existence of graphite in the composite, which is further confirmed by the Raman result (Fig. 2), The most prominent features in the Raman spectrum of graphite are the so-called G band appearing at 1570 cm⁻¹ and the D band at about 1347 cm⁻¹. Besides, a symmetrical single 2D peak at around 2691 cm⁻¹ is also observed, which stems from the second order of the zone-boundary phonons [22].

The morphology of dried sewage sludge before annealing is bulk-shaped with the size of ca. 20 μ m (Fig. 3a). After annealing, irregular nanoflakes (ca. 140 nm thickness) decorated by some nanoparticles are observed (Fig. 3b). After milling, size-decreasing nanoparticles are formed (Fig. 3c). Fig. 3d-f shows the SEM images of milling composites S1, S2, and S3, which have the analogous morphologies.



Figure 1. XRD patterns of as-prepared samples S0, S1, S2 and S3.



Figure 2. Raman spectrum of the composite S2.



Figure 3. SEM images of (a) dried sewage sludge, (b) annealed sewage sludge, (c) S0, (d) S1, (e) S2, (f) s3; (g) TEM, (h) HRTEM images, (i) SAED pattern of S2; (j-m) elemental mappings of S2.

The size of samples shows an increased trend (500-700 nm) along with the increase of graphite probably due to the adhesion of graphite during the milling process. The detailed microstructure of

sample S2 is further characterized by TEM (Fig. 3g), the observed product displays a well-defined structure with 90 \pm 10 nm average length by 60 \pm 5 nm average width. Besides, some particles break at the fringe area to form small nanoparticles (ca. 30 nm) during the milling process. The high-resolution TEM (HRTEM) image in Fig. 3h shows the lattice interspacing of 0.425 and 0.337 nm, attributing to the SiO₂ (100) and graphite (002) crystal planes, respectively. In addition, the corresponding SAED pattern (Fig. 3i) shows the ordered lattice structure consistent with the (100), (101), and (201) planes of the hexagonal SiO₂. The elemental mappings of the composite (Fig. 3j-m) indicates the relatively homogeneous distribution of Si, C, and O elements, which is beneficial to increase electronic or ionic transport when the composite is used as an anode material for LIBs [16, 18, 23].



Figure 4. (a) Rate capabilities of samples, (b) the initial discharge/charge curves of S2, and (c) cycling performance of samples.

The electrochemical properties of the as-prepared samples are investigated as LIBs anodes in the voltage range of 0.01-3.0 V (vs. Li⁺/Li). Fig. 4a compares their rate capabilities at the current densities from 100 to 5000 mAg⁻¹. Sample S0 exhibits reversible capacities of 248, 181, 161, 124, 97, and 57 mAh g⁻¹ at the corresponding densities. In contrast, the rate performance of sewage sludge is significantly enhanced by hybridization with graphite. In particular, Sample S2 achieves reversible capacities of 489, 354, 268, 212, 167, and 127 mAh g⁻¹ at the current densities from 100 to 5000 mAg⁻¹, which are higher than those of S1 and S3. Moreover, the sample S2 exhibits good capacity recovery of 377 mAh g⁻¹ when the current density was abruptly returned to 100 mAg⁻¹ after testing under the large current density, suggesting its excellent rate stability. Fig. 4b shows the initial charge and discharge curves of samples S0-4 at the current density of 1000 mAg⁻¹, and sample S2 exhibits the highest discharge and charge capacities of 467 and 198 mAh g⁻¹. The large irreversible capacity loss is probably attributed to the formation of the solid electrolyte interface (SEI) layer [8, 14, 23]. Fig. 4c

shows the cyclic performance of the as-prepared samples at the current density of 1000 mAg⁻¹. The discharge capacity of S0 decreases successively to only 68 mAh g⁻¹ after 500 cycles owing to the continuous structural damage. In contrast, the discharge capacity of the hybrids with less graphite (S1) is 139 mAh g⁻¹ after 500 cycles. Increasing the graphite ratio, sample S2 delivers a much higher capacity of 244 mAh g⁻¹ at 500th cycles with a Columbic efficiency of nearly 100%, demonstrating its excellent cycling performance. However, sample S3 exhibits a 500th-cycle capacity of 166 mAh g⁻¹, indicating that excessive graphite deteriorates the lithium storage performance of sewage sludge.

To further evaluate the electrochemical properties of the sewage sludge sample as LIBs anodes, the cyclic voltammetry (CV) curves of sample S2 are detected at a scan rate of 0.01 mV s⁻¹ (Fig. 5a). The cathodic peak at 0.6 V in the first cycle disappears in the following cycles, indicating the electrolyte decomposition and the SEI formation [8, 14, 19, 23]. Another reduction peak at ca. 0.1 V is related to the Li-Si alloy process [16, 19, 23]. Subsequently, the broad anodic peak at ca. 1.2 V is corresponding to the delithiation process of the active materials [8, 19, 23]. After the first cycle, the CV curves are nearly overlapped, indicating its good reversibility.



Figure 5. (a) CV curves, (b) initial discharge/charge curves, (c) cycling performance, and (d) Nyquist plots of S2 electrode.

Fig. 5b shows the initial three discharge/charge curves of S2 electrode at the current density of 100 mA g^{-1} . The observed voltage slope at about 0.6 V corresponds to the electrolyte decomposition and SEI formation [8, 14, 19, 23]. The first discharge and charge capacities of S2 electrode are 711 and 470 mAh g^{-1} , respectively, with a good initial Coulombic efficiency of 66%. After 100 cycles, the S2 electrode presents stable reversible capacity of 433 mAh g^{-1} with 92% capacity retention (Fig. 5c). These results indicate that sample S2 originated from sewage sludge has superior electrochemical performance compared to many reported SiO₂-based anodes (Table 1).

Materials	Cycling stability	Rate capability	Reference
SiO ₂ from glass waste	144 mA h g^{-1} after 50	75 mAh g^{-1}	[9]
- 0	cycles at 7 mA g^{-1}	at 100 mA g^{-1}	
Electrospun SiO ₂ /C fibers	$465 \text{ mA h g}^{-1} \text{ after } 50$	240 mAh g^{-1}	[14]
	cycles at 50 mA g^{-1}	at 500 mA g ⁻¹	
Hollow SiO ₂ nanocubes	919 mA h g^{-1} after 30	-	[8]
	cycles at 100 mA g^{-1}		
SiO ₂ /mesoporous carbon	550 mA h g^{-1} after 12	-	[15]
	cycles at 50 mA g^{-1}	1	
SiO ₂ /polyacrylonitrile/C	$430 \text{ mA h g}^{-1} \text{ after } 115$	352 mAh g^{-1}	[24]
	cycles at 55 mA g ⁻¹	at 440 mA g^{-1}	
Hollow SiO ₂ nanorods	332 mA h g^{-1} after 50	-	[25]
	cycles at $1/mAg^{-1}$		[0.6]
$S1O_2$ nanoparticles/C	500 mA h g^{-1} after 50	-	[26]
SiO /C/american	cycles at 50 mA g 251 mA h s^{-1} ofter 200	$76 \text{ mAb } a^{-1}$	[27]
SIO ₂ /C/graphene	231 IIIA II g after 200	70 IIIAII g	[27]
SiO. from sewage	$433 \text{ mA h } \text{g}^{-1} \text{ after } 100$	$127 \text{ mAh } a^{-1}$	This work
sludge/graphite	435 mA ng and 100 mA g^{-1}	at 5000 m Δ g ⁻¹	THIS WORK
studge/graphite	244 mA h s^{-1} after 500	at 5000 mA g	
	cycles at 1000 mA σ^{-1}		
	- J		

Table 1. Comparison of electrochemical performance of various reported SiO₂-based anodes.

-: not available

The electrochemical kinetics of S2 electrode is further measured by the electrochemical impedance spectra and fitted by the equivalent circuit. As shown in Fig. 5d and summarized in Table 2, the diameters of the depressed semicircles in high-medium frequency areas evidently become smaller after 100 cycles, indicating the decrease of the contact and charge-transfer impedances (R_{ct}), owing to the formation of stable interface between electrodes and the electrolyte. Likewise, similar phenomenon was also observed in many previous reports [17, 18, 24].

Table 2. Impedance parameters derived from the equivalent circuit models of the S2 electrode.

Cycling number	$R_s[\Omega]$	$R_f[\Omega]$	$R_{ct}[\Omega]$
1 st	2.1	6.4	37.5
100 th	2.0	6.1	10.4

4. CONCLUSIONS

Sewage sludge is effectively converted to a promising LIBs anode by a simple annealing method combined mechanical milling with a handful of graphite. The prepared sewage sludge sample

hybridized with appropriate dosage of graphite exhibits good electrochemical performance as LIBs anodes. It delivers stable reversible capacity of 433 mAh g^{-1} after 100 cycles at the current density of 100 mA g^{-1} . At a high current density of 1000 mA g^{-1} , the reversible capacity is still stabilizing at 244 mAh g^{-1} after 500 cycles with a Columbic efficiency of nearly 100%, demonstrating that the successfully recycled waste sewage sludge is a potential LIBs anode.

ACKNOWLEDGEMENTS

This work was supported by National Natural Science Foundation of China (No. 21203116), Scientific Research Fund of San-qin Scholar (No. BJ11-26), and Scientific Research Fund of Shaanxi University of Science and Technology (No. XSG(4)006).

References

- 1. L. Croguennec and M. R. Palacin, J. Am. Chem. Soc., 137 (2015) 3140-3156.
- 2. B. Scrosati, J. Hassoun and Y. K. Sun, Energ. Environ. Sci., 4 (2011) 3287-3295.
- 3. J. C. Bachman, S. Muy, A. Grimaud, H. H. Chang, N. Pour, et al. Chem. Rev., 116 (2016) 140-162.
- 4. X. Shi, H.H. Song, A. Li, X. H. Chen, J. H. Zhou et al. J. Mater. Chem. A., 5 (2017) 5873-5879.
- 5. X. Liu, J. Q. Huang, Q. Zhang and L.Q. Mai, Adv. Mater., 29 (2017).
- 6. S. L. Candelari, Y. Y. Shao, W. Zhou, X. L. Li, J. Xiao, et al. Nano Energy., 1 (2012) 195-220.
- 7. W. S. Chang, C. M. Park, J. H. Kim, Y. U. Kim, G. Jeong, et al. *Energy Environ. Sci.*, 5 (2012) 6895-6899.
- 8. N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu and Q. W. Chen, Sci. Rep., 3 (2013) 259-264.
- 9. A. Prasath and P. Elumalai, ChemistrySelect., 1 (2016) 3363-3366.
- 10. B. Gao, S. Sinha, L. Fleming and O. Zhou, Adv. Mater., 13 (2001) 816-819.
- 11. Q. Sun, B. Zhang and Z. W. Fu, Appl. Surf. Sci., 254 (2008) 3774-3779.
- 12. Z. Favors, W. Wang, H. H. Bay, A. George, M. Ozkan and C. S. Ozkan, *Sci. Rep.*, 4 (2014) 4605-4611.
- M. Sasidharan, D. Liu, N. Gunawardhana, M. Yoshio and K. Nakashima, J. Mater. Chem., 21 (2011) 13881-13888.
- 14. Y. R. Ren, Bo. Yang, H. M. Wei and J. N. Ding, Solid State Ionics., 292 (2016) 27-31.
- 15. S. Hao, Z.W. Wang and L. Q. Chen, Mater Design., 111 (2016) 616-621.
- L. Y. Li, P. C. Liu, K. J. Zhu, J. Wang, G. A. Tai and J. S. Liu, *Electrochim. Acta.*, 235 (2017) 79-87.
- 17. J. L. Cui, F. P. Cheng, J. Lin, J. C. Yang, K. Jiang, et al. Powder. Technol., 311 (2017) 1-8.
- 18. X. L. Liu, Y. X. Chen, H. B. Liu and Z. Q. Liu, J. Mater. Sci. Technol., 33 (2017) 239-245.
- 19. M. L. Jiao, K. L. Liu, Z. Q. Shi and C. Y. Wang, Chemelectrochem., 4 (2017) 542-549.
- 20. Z. N. Yuan, N. Q. Zhao, C. S. Shi, E. Z. Liu, C. N. He and F. He, *Chem. Phys. Lett.*, 651 (2016) 19-23.
- 21. X. J. Zhou, J. L. Zhang, H. X. Wu, H. J. Yang, J. Y. Zhang and S. W. Guo, J. Phys. Chem. C., 115 (2011) 11957-11961.
- 22. M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, et al. J. Am. Chem. Soc., 131 (2009) 3611-3620.
- 23. M. Q. Li, Y. Yu, J. Li, B. L. Chen, X. W. Wu and Y. Tian, P. Chen, *J. Mater. Chem.* A., 3 (2014) 1476-1482.
- 24. M. Q. Li, K. Li, Y. Zhao, Y. G. Zhang, D. osselink and P. Chen, *J. Power Sources.*, 240 (2013) 659-666.
- 25. G. Yoo, C. Kim, B. Jang, S. Yang and J. Son, J. Nanosci. Nanotechno., 15 (2015) 8773-8776.

26. Y. Yao, J. Zhang, L. Xue, T. Huang and A. Yu, *J. Power Sources*, 196 (2011) 10240-10243. 27. Y. Ren, H. Wei, X. Huang and J. Ding, *Int. J. Electrochem. Sci.*, 9 (2014) 7784-7794.

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