Supplementary Information for

Preparation of Sb nanoparticles in molten salt and their Potassium

Storage performance and Mechanism

Zheng Yi, Ning Lin, Wanqun Zhang, Weiwei Wang, Yongchun Zhu* and Yitai Qian*

Department of Chemistry and Hefei National Laboratory for Physical Science at Micro-scale, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: ytqian@ustc.edu.cn, <u>ychzhu@ustc.edu.cn</u>.



Fig. S1 The SEM images of the bulk Sb powders, which is directly purchased from Aladdin Co. with any treatment.



Fig.S2 (a) The XRD pattern of the crude product obtained at 75 °C without any washing treatment, and (b) the optical photograph of the obtained high-yield Sb nanoparticles at 80 °C and 100 °C.

To understand the reaction process for fabricating crystalline Sb nanoparticles, the XRD pattern of the crude product obtained at 75 °C without any washing treatment is given, as shown in Fig. S2a (Supporting Information). A weak diffraction peak located at 28.7° is detected, which could be corresponding to Sb phase. The more intensive diffraction peaks labelled as "solid circle" and "square" are assigned to the excess reagent, antimony chloride and micron-sized Al powder, respectively. Because the AlCl₃ chloride melt is intensively hydrolysis with the moisture in the air, the obtained XRD pattern signal is relatively weaker. Even so, the by-product of AlCl₃ is detected. According to the above products, it is reasonable to propose a reaction mechanism in the molten salt system as equ. (1).

Al + SbCl₃ \rightarrow Sb + AlCl₃ H^{θ} = - 322 kJ mol⁻¹, ΔG^{θ} = - 302.02 kJ mol⁻¹ (1)

In this closed response system at 75 °C, liquid-phase SbCl₃ environment ensures that homogeneous nucleation is the leading form in the resultant, hence produce the monodispersed Sb nanoparticles. In addition, according to the calculation of the free energy of the reaction (1), it can be seen that this process is thermodynamically spontaneous and highly exothermic. On the other hand, the molten salt is like a sea, which can homogenize the local autogenic heat to create a homogeneous system in the reactor.¹ So, this homogeneous system maintains the homogeneous growth of the Sb nanoparticles. As a result, homogeneous nucleation and growth endow the reaction generating of monodispersed Sb nanoparticles.



Fig. S3. SEM images of the different reducing agents. (a) Al, (b) Mg, (c) Zn and (d) Fe.



Fig. S4 SEM images and XRD patterns of the obtained Sb products by employing different reducing agents. (a) Mg, (b) Zn and (c) Fe.

From Fig.S3 and S4, it can be seen that the related experiment could be extended by utilizing different active metals, such as Mg, Zn and Fe (Fig. S3, Supporting Information) etc., as reducing agents. The morphology and structure of the obtained products are exhibited in Fig. S4 (Supporting Information). The XRD results (Fig.S4d, Supporting Information) show that the obtained products are all indexed to a Sb phase. And the particle sizes (Fig.S4a-c, Supporting Information) are also at nano-level, when reduced by Mg, Zn and Fe, respectively.



Fig.S5 Schematically illustration the depotassiation mechanism of Sb nanoparticles.



Fig.S6. Comparison of the potassium storage capacity of bulk Sb and Sb nanoparticles at different current densitie from 100 to 2000, and return to 100 mA g^{-1} .



Fig.S7 (a) SEM, (b) TEM images, (c) XRD, (d) Raman spectrum of the Sb@RGO composite obtained by a hydrothermal method.



Fig. S8 TG curve of the Sb@RGO composite at air.

In the curve, the Sb nanoparticle oxidized to Sb_2O_4 after 450 °C. So, about 550 °C, the residue is Sb_2O_4 .² Therefore, according to the following equation (1),³ the graphene content is tested to be approximately 42 wt.% by thermogravimetry analysis.



Fig. S9 XPS results of the Sb@RGO composite obtained by a hydrothermal method, (a) C1s and (b) Sb 3d.

As presented in Fig. S7a-b, the obtained Sb@RGO composite shows a uniform dispersion of Sb nanoparticles into graphene, formation of a close-knit Sb@RGO alliance. Fig. S7c is the XRD pattern of the Sb@RGO composite. It can be seen that the main diffraction peaks of the Sb@RGO composite are in agreement with the characteristic peaks of Sb. It is noteworthy that the Sb nanoparticle in the composite can be partly surface oxidized when the composite fabricated by a hydrothermal treatment. The caused surface oxidation of Sb could be possibly attributed to the fact that the interface energy of the nano Sb is comparatively high. As a result, in the presence of water in a hydrothermal process, the nano Sb could be easily oxidized, which is detected by XRD pattern (Fig. S7c). According to the reported result by J. Bao et al 4 and the intensity ratio of the strongest XRD peaks between Sb and Sb₂O₃, the Sb₂O₃ content is about 1.2 wt.%. The graphene content is tested to be approximately 42 wt.% by the thermogravimetry analysis (Fig. S8, Supporting Information). Raman spectra of the Sb@RGO composite are measured. As shown in Fig.S4d, the Sb@RGO composite exhibits two clear peaks at 1350 and 1588 cm⁻¹, which are designated as the D and G bands of the graphene, respectively. The value of D peak is relatively high, which may be due to the fact that Sb nanoparticles dispersed into the interlamination of graphene, giving a higher extent of disorder. Furthermore, high D/G intensity ratio of 1.1 suggests the oxygen functional groups of graphene

oxide have been removed mostly in the hydrothermal process.⁵⁻⁶ To further investigate the chemical composition of the Sb@RGO composite, XPS measurements are carried out. As presented in Fig. S9a (Supporting Information), the C 1s spectra mainly present two peaks containing of the C-C and C-O bonding, respectively. The C-C bonding is much higher than that of C-O bonding, suggesting that numbers of oxygenated functional groups are largely reduced during preparing process. For the Sb 3d (Fig. S9b, Supporting Information), there are two antimony environments: Sb³⁺ at 540.1 and 530.8 eV, and Sb⁰ at 537.8 and 528.5 eV, corresponding to Sb₂O₃ and metallic Sb, respectively. Because Sb₂O₃ is easily enriched at the surface of Sb nanoparticles in the hydrothermal process, the amount of Sb₂O₃ would be overmeasured than its actual amount.



Fig. S10 Comparison of the potassium storage coulombic efficiency of bulk Sb, Sb nanoparticle and the Sb@RGO composite at a current density of 200 mA g⁻¹. It can be seen that the first coulombic efficiency of bulk Sb is the highest. However, the coulombic efficiency in cycling apart from the first cycle is lower. The coulombic efficiency of Sb nanoparticle after first cycle gradually decreases. By contrast, the Sb@RGO composite has higher and stable coulombic efficiency after first cycle.



Fig.S11. the corresponding capacity retention of the Fig.4b at different rates of the Sb@RGO composite at current densities from 100 to 5000, and return to 100 mA g^{-1} . Note that the capacity retention ratio is calculated based on the second discharge capacity.



Fig. S12 the charge/discharge curves at current densities from 100 to 2000 mA g^{-1} .



Fig. S13 Comparison of the potassium storage capacity of the Sb@RGO composite with the reported alloying-type anode materials for PIBs at different current densities.

Materials	Current	Cycle	Capacity	Reference
	density	number		
Milled Sn/C	25 mA g ⁻¹	30	150 mA h g ⁻¹	Chem. Commun., 2016, 52,
composite				9279
Porous Sn/C	50 mA g ⁻¹	100	276.4 mA h	J Mater Chem A, 2018, 6,
composite			g-1	434
Red P/C	50 mA	50	323.5 mA h	J. Power Sources 2018, 378,
composite	g ⁻¹		g-1	460
Black P/C	50 mA	50	270 mA h g ⁻¹	J. Mater. Chem. A, 2017, 5,
composite	g ⁻¹			23506
Sb/C composite	1 A g ⁻¹	50	225 mAh g ⁻¹	Nanoscale, 2018,
				DOI: 10.1039/C8NR00237
				A
Graphene	200 mA	40	300 mAh g^{-1}	This work
supported Sb	g-1			
nanoparticles	500 mA	200	210 mAh g ⁻¹	
	g-1			

Table.S1 Comparison of the potassium storage capacity of the Sb@RGO composite

 with the reported alloying-type anode materials for PIBs at different current densities



Fig. S14 The SEM image of the Sb nanoparticles electrode after first discharge/charge process.

To detect whether the Sb nanoparticles still remain in their initial nanostructure after cycling, we obtain a SEM image of the Sb nanoparticles electrode after first discharge and charge process, as seen Fig.S14. It can be seen that these nanoparticles with size less-than 100 nm could be the cycled Sb nanoparticles. So, we think that the Sb nanoparticles still remain in their initial nanostructure after cycling.



Fig.S15. (a) GITT voltage profiles of the Sb@RGO composite electrode at 40 mA g⁻¹ during the second cycle, (b) comparison of the potassium ion diffusion coefficients in bulk Sb, Sb nanoparticle and the Sb@RGO composite electrode derived from the GITT voltage profiles.

To monitor the reaction resistance evolution of the bulk Sb, Sb nanoparticle and Sb@RGO composite, the galvanostatic intermittent titration technique (GITT) measurement is further carried out at 40 mA g⁻¹ during the second cycle, as presented in Fig.3c and Fig.S15a (Supporting information). In this quasi-equilibrium potentials, the discharge overpotential of both samples decreases with the state of discharge, which means that the potassium diffusion length was becoming shorter.

While the charging overpotential increases with the state of charge, which is attributed to the volume contraction during potassium extraction worsen the contact between particles.⁷⁻⁸ In addition, the diffusion coefficient of potassium in these Sb-based anodes for PIBs has been extracted from the GITT for the second cycle, as contrastively presented in Fig.S15b. The potassium diffusion coefficient in Sb@RGO composite anode is about $0.2 \sim 2.8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, high than that of bulk Sb as well as Sb nanoparticle. The higher diffusion coefficient also suggests the good potassium storage performance, as contrastively discussed in Fig.4a.



Fig. S16 The CV profiles of the Sb@RGO composite electrode at different scan rate from 0.2 to 0.7 mV s⁻¹, and (b) the corresponding log(i, current)-log(v, scan rate)curves of the Sb@RGO composite electrode at the typical anodic peak. (c) Capacitive (red) and diffusion-controlled (white) contribution to charge storage of Sb@RGO composite at 0.5 mV s-1, and (d) normalized contribution ratio of capacitive (red) and diffusion-controlled (blue) capacities at different scan rate.

To explain the good rate performance of the Sb@RGO composite, we also analyse the redox pseudocapacitance-like contribution in the Sb@RGO electrode by investigating the kinetics behavior to separate the diffusion controlled capacity and capacitive capacity. Fig.S16a (Supporting information) is the CV curves with similar shapes measured at various scan rates from 0.2 to 0.7 mVs⁻¹. Based on the relationship between the current (*i*) and scan rate (*v*) as equivalently formulated in equ. (3), the b-value could be determined by plotting of the log(*i*)-log(*v*) curves.⁹⁻¹¹ $i = a * v^b \qquad (3)$

After calculation, the b-value of the Sb@RGO composite is about 0.71, much higher than that of pure Sb particles (Fig.S17, Supporting information). The higher b-value suggests that the charge storage of the Sb@RGO composite is dominated by both diffusion controlled and capacitive capacity. The ratios of potassium ion capacitive contribution is further quantified by separating the current response *i* at a fixed potential (V) into capacitive effects (k_1v) and diffusion-controlled reactions ($k_2v^{1/2}$), ¹¹ according to the equ.(4):

 $i(V) = k_1 v + k_2 v^{1/2}$ (4)

By determining both the k_1 and k_2 constants, the fraction of the current from capacitance capacity can be distinguished. Fig.S16c shows the typical voltage profile at 0.5 mV s⁻¹ contains of capacitive current (red region) in comparison with the total current. A quantitative capacitive contribution of about 45.6 % is calculated for the Sb@RGO composite anode. The proportion of capacitive contribution can further enlarge when the scan rate increased to 0.7 mV s⁻¹. This pseudocapacitive contribution may be attributed to the coating of RGO with high surface area or high porosity, which help for the Sb anode obtain a higher rate capacity.



Fig. S17 The CV profiles of the Sb nanoparticle electrode at different scan rate from 0.2 to 0.7 mV s⁻¹, and (b) the corresponding log(i, current)-log(v, scan rate) curves of the Sb nanoparticle electrode at the typical anodic peak.

Fig. S18. Electrochemical performances of the Sb@RGO composite (with RGO content of 20.8 wt.%) for SIBs, (a) CV curves at a scanning rate of 0.1 mV s⁻¹, (b) charge/discharge curves at a current density of 0.2C, (c) galvanostatic charge/discharge capacity at a current density of 0.2 C, (d) rate capacity at current densities from 0.2C to 5C and (e) galvanostatic discharge capacity for 200 cycles at a current density of 1C (1C = 660 mA g⁻¹).

Apart from the good potassium storage performance, the Sb@RGO composite also exhibit excellent sodium storage capacity, as shown in Fig.S18 (Supporting information). The composite with RGO content of 20.8 wt.% can deliver average reversible capacity of about 533.8, 471.5 and 415.2 mAh g⁻¹, at current rate of 0.2, 0.5 and 1 C (1C = 660 mA g⁻¹), respectively. Even at 2 and 5 C, the capacity can be retained at about 373.2 and 287.2 mAh g⁻¹, after 40

and 50 cycles, respectively. When the half cell is further discharged at 0.2 C to 80 cycles, a capacity of 508 mAh g–1 can still be maintained. The good rate capability and cycling performance of the Sb@RGO composite are further investigated at a current density of 1 C for 200 cycles. As shown in Fig.S18e (Supporting information), the Sb@RGO composite can maintain a capacity of 383.5 mAh g⁻¹ even at this condition.

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