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ARTICLE TYPE

rGO /nano Sb composite: A high performing Anode material for Na⁺ ion Batteries and Evidence for Formation of Nanoribbons from Nano rGO sheet during Galvanostatic Cycling

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Lithium ion batteries exhibit high energy and power densities thereby making them as a promising power sources for multifarious applications. However, the abundance of Lithium (Li) is one of the major critical issues for using in Li battery technologies. Therefore, for large scale applications sodium ion battery is one of the apt alternatives for portable electronics instead of expensive Li ion battery. One of the challenging issues in Na⁺ ion battery is the difficulty to understand the chemistry involved in view of the large size of the Na⁺ ion as compared to Li⁺ ion and makes the alloying/dealloying difficulty during cycling. Hence, in this present work, we explore an innovative concept of storing Na⁺ ions in the reduced graphene oxide/ antimony (Sb) metal composites. Such concept of storing Na⁺ in the rGO/Sb composite is one of the simplest ways to enhance the electrochemical performance of metal based anodes for sodium ion batteries. Further, it is seen that Nano rGO sheet transforms to Nanoribbons upon galvanostatic cycling as evidenced by TEM.

Introduction

Currently energy storage is an important challenge to overcome the present day's energy demand and moreover, storing energy in greener way is too important to create zero carbon emission world. Lithium ion batteries are suitable energy storage device and recently it has dominated the portable electronic markets due to its high energy and power density. However, the cost and depletion of lithium source is a big hurdle to produce these batteries for electric vehicular applications. A possible alternative chemistry to overcome the energy crisis is sodium ion chemistry which is considered to be a promising candidate over lithium ion batteries. Sodium ion cells possess advantages such as high¹ voltage (~3.5V) operates well at room temperature, inexpensive electrode and electrolyte active materials and more significantly it is easily portable.

Recently, Na ion chemistry has been explored by few research groups²⁻⁴, however, all these studies have been mainly focused on cathode materials. As reported by X. Ma et al⁵ electrode structure does not work well for Na ion alloying/dealloying. Therefore, it is pertinent to explore an appropriate anode material to store Na⁺ ions as there are only very few reports available for storing Na⁺ ions. D. A. Stevens et al⁶ first reported that hard carbon based anode materials exhibiting a reversible capacity of 300 mAhg⁻¹ Vs Na/Na⁺. However, the performance of hard carbon based materials is not satisfactory and cycle life is also poor when it is used as an anode material in sodium ion batteries. Apart from

this, most significantly amorphous TiO₂⁷, Li₄Ti₅O₁₂⁸, NaTi₂(PO₄)₃⁹, P2-Na_{0.66}[Li_{0.22}Ti_{0.78}]O₂¹⁰, Sb/C¹¹, SnSb/C¹², microspheric Na₂Ti₃O₇ tiny nanotubes¹³, SnO₂@graphene nanocomposites¹⁴, Sb/Graphene¹⁵ and organic based anode materials^{16, 17} have been reported as anode materials for Na ion technologies. However, few of the aforesaid systems suffered from several drawbacks viz., low reversible capacity, poor capacity retention, large irreversible capacity in the first cycle and low columbic efficiency but some of them actually show good performance^{8,12}. Recently, graphene based materials¹⁵ have been explored for energy storage applications because of its special structure (monolayer of graphene) which exhibits excellent properties such as good chemical stability and outstanding electronic transport properties^{18, 19}. Apart from these unique properties, it acts as a conductive carbon network to host active materials for energy storage applications. However, large irreversible capacity in the first cycle and also restacking of graphene sheets during cycling leads to poor capacity retention²⁰ especially in lithium based energy storage systems. Graphenes produced from physical methods do not show any defects in its structure but prepared from chemical oxidation-reduction methods produce high degree of defects which enhances the conductivity. Defect related graphene phases are usually prepared from graphene oxide (GO) (which consists of highly oxygenated, bearing hydroxyl, epoxide, diol, ketone and carboxyl functional groups²¹) through modified Hummers method^{22, 23}. The chemical reduction of GO removes the oxygen containing functional groups²⁴ however, these reduction does not form graphene but it

forms partially reduced graphene oxides which is non-stoichiometric and possess defects indicating the presence of disordered graphene oxides. With these unique properties, reduced graphene oxides (rGO)²⁵ have received much attention instead of graphene because it also possess high conductivity²⁶ of 16000 S/m². Similar to graphene, reduced graphene oxides also act as an excellent host for active materials²³ during cycling due to its high flexibility. Addressing the disadvantages of the above mentioned anode materials, we present herein for the first time a new concept of storing Na⁺ ions into the Sb anode supported with reduced graphene oxides (rGO) matrix which exhibits high reversible capacity and cycleability. The mechanism of alloying / dealloying of Na⁺ ion in the Sb is supported by highly conductive reduced graphene oxide (rGO) matrix.

Experimental

Modified Hummers method has been adopted for preparing graphene oxides (GO)^{22, 23}. The rGO/Sb composite was prepared by reduction method using NaBH₄ as reducing agent. In a typical experiment, 1.5g of graphite oxide (synthesized by using Hummers method) was dispersed in 50 ml of water and subsequently added 7 g of SbCl₃ solution. With this mixture solution, 1g of NaBH₄ and 0.5g of CTAB were added under continuous stirring. For the preparation of bare Sb particle the same procedure was repeated but without adding GO. After exposure to ultrasound from an ultrasonic bath (Model DCR-TRV33E, 230V, 50 Hz) for 30 min, the black-grey mixture was collected by filtration. After washing with deionized water in an attempt to remove excess Cl⁻ ions as well as surfactant and other ions, the rGO/Sb composite was obtained by drying for 24 h in vacuum.

TG/DTA analysis of the rGO/Sb was examined from 0°C to 780°C with a heating rate of 20°C per minute in air atmosphere to understand the thermal decomposition behaviour. The synthesized GO and rGO/Sb composites was characterized in a x-ray diffractometer ('Xpert PRO PANalytical PW 3040/60 'X'Pert PRO') at a scan rate of 2°min⁻¹ using Cu-K α radiation (λ = 1.5418Å), while the voltage and current were held at 40 kV and 20 mA (2 θ = 10–80°). The morphology and microstructure of the composites were characterized in a scanning electron microscope (SEM HITACHI S-3000 H, Japan) and transmission electron microscopy (TEM, FEI-Tecnai-20 G2). Raman spectra were recorded for the synthesized materials in a Renishaw InVia Laser Raman Microscope with He-Ne laser (633 nm).

The anode was prepared by mixing 80 wt% prepared composites, 10 wt% Super-P carbon and 10 wt% polyvinylidene fluoride (PVdF) binder in N-methylpyrrolidone (NMP) solvent to form a homogeneous slurry. Similar procedure was adopted for the preparation of Sb anodes. The slurry was coated on copper foil and dried under ambient condition. 18 mm diameter circular discs were punched out and dried under vacuum at 120°C for 12h. The mass loading of the active materials for Sb and rGO/Sb are 1.02 mg/cm² and 1.05 mg/cm² respectively. Finally, coin cells of 2032 type were assembled inside an argon filled glove box using the prepared anode as working electrode, sodium foil as reference electrode, celgard 2400 as the separator and 1M NaClO₄ in 1:1 EC/PC as electrolyte. Charge-discharge studies of

the coin cells were carried out using a programmable battery tester at a constant current of 131 mA g⁻¹ for 50 cycles in the potential range of 0.01–1.5V. Cyclic voltammogram were recorded using an EG&G instruments (Princeton Applied Research) at a scan rate of 0.1 mVs⁻¹ between 0.01 and 1.5V. Electrochemical Impedance Spectra were measured by using an EG & G instruments Model 5210 with an AC voltage signal of 5 mV and the frequency range was between 100 KHz and 5 mHz.

Results and Discussion

Fig. 1 shows the TG/DTA curve of bare Sb and rGO/Sb composite. Approximately 6% weight loss occurs in the TG curve of bare Sb which corresponds to loss of superficial water molecules. After this region 5.48% weight gain (from 290 - 512°C) occurs due to the oxidation of Sb to Sb₂O₄ corresponding to an exothermic peak observed in DTA curve. The first weight loss region in the TG curve of rGO/Sb composite is approximately 4% corresponding to the loss of water molecules in the bulk rGO material. The next weight loss region between 100 and 425°C is due to the loss of rGO in the synthesized composites leads to 15% weight loss. After this region, TG curve becomes flat which means that there is no weight loss in the synthesized composites. This confirms that the synthesized composites contain 9.52% of rGO.

Fig. 2a depicts the XRD patterns of Sb and rGO/Sb composites. The inset is the XRD pattern of GO synthesized by Hummers method. The strong and sharp peak for GO is observed at 2 θ = 10.7° with the d-spacing of 8.830 Å. The high intensity peak observed for Sb at 2 θ = 28.16° which is in agreement with ICDD pattern no. 00-001-0802. After the reduction of SbCl₃ and GO mixture, the peaks centered²⁷ at 2 θ = 25.91° confirms the formation of rGO from GO by reducing with NaBH₄. The finger print peaks at 2 θ = 28.16°, 40.05°, 42.10° and 51.7° confirmed the formation of Sb particles in both pristine and composites. The sharp peaks are observed which indicate that the synthesized Sb particles are highly crystalline. The absence of peak at 2 θ = 10.7° in the composites confirmed that the synthesized composite doesn't contain any GO phases thereby indicating that the reducing agent NaBH₄ completely reduces the GO. The peak intensity of rGO (9.52% of rGO in the synthesized composites which is confirmed by TGA) appears too small as compared to Sb because its composition is less in the composites.

Laser Raman scattering is a sensitive tool to analyze the graphite and graphene based materials. Usually we observe two major bands²⁸ in the Raman spectra i.e., D (κ point phonons of A1g symmetry) and G band (phonons of E_{2g} symmetry) which characterize the vibration of defect related SP³ bonded carbon atoms and SP² carbon atoms respectively. Fig. 2b presents the laser Raman spectra of GO and rGO/Sb composites. D and G bands are observed for GO and rGO at 1328, 1596 cm⁻¹ and 1334, 1594 cm⁻¹ respectively. However, after the reduction of GO with NaBH₄, the intensity of D band increases which is attributed to the formation of rGO in the synthesized composites. The ratio of D/G for GO is 1.05 and for rGO/Sb is 1.28 respectively. After reduction with NaBH₄ the D band becomes stronger as well as too broader than 'D' band observed in GO suggesting that high degree of disorder in graphene layers results

more defects²⁹ which are created in rGO during functionalization process of GO. The second order 2D band is observed at 2700 cm^{-1} but we can't determine the number of graphene layers using this band but this is useful to know about the electronic effects of graphene related materials^{30, 31}. This kind of increase in intensity and broadening of D band creates more defects in the rGO matrixes which generally increases the conductivity.

Fig. 3a and b represent the SEM images of Sb, GO and rGO/Sb composites. The synthesized GO's appear as flakes and aligned as an array of sheets arranged together. The SEM image of Sb particle shows spherical morphology with agglomeration. In the composite, the Sb particles are of spherical shape morphology which is controlled by adding the surfactant, CTAB. Furthermore, the morphology of the active particles greatly influences the electrochemical performance of the metal particle during galvanostatic cycling. Hence, it is presumed that such type of spherical morphology should enhance the electrochemical performance of the synthesized material during cycling.

The SAED (Fig. 3c) pattern of rGO/Sb composites confirms the presence of Sb particles anchored on the surface of rGO sheets. We observed two ring patterns in which inner ring corresponds to (113) plane and outer ring corresponds to (002) plane of Sb particle and rGO respectively. TEM image (Fig. 3d) of rGO/Sb composites clearly shows the spherical shape morphology of Sb particles which is fastened on the surface of rGO sheets. The size of the Sb particles varies from 10 to 20 nm.

In order to examine the Na^+ ion alloying/dealloying behaviour of rGO/Sb composites, we carried out galvanostatic cycling studies (Fig. 4a) between the potential limits of 0.01 and 1.5 V at a current density of 131 mA g^{-1} . The initial charge capacity for Sb, rGO and rGO/Sb are 601, 511 and 641 mAh g^{-1} respectively. We observed large irreversible capacity for pristine rGO and Sb anodes because of its high surface area which leads to the formation of thick SEI layer on its surface. The charge/discharge curves exhibit two plateaus at ~ 0.76 and 0.42 V ascribed to the behavior of Na^+ ion alloying/dealloying reaction with Sb anodes. This can be ascribed to the alloying/dealloying reaction of Na^+ ion with Sb particles leading to the formation of Na_3Sb which is in good agreement with J. Qian et al¹⁰. The intercalation/deintercalation of Na^+ ions in rGO sheets may occur in two ways according to J. R. Dahn and Y.H. Liu et al³²⁻³⁴. Similar to Li^+ ion intercalation, the Na^+ ions also may be adsorbed on both sides of reduced graphene sheets and forms two layers of Na^+ ion on each sheet leading to the formation of Na_2C_6 . On the other hand cavities between reduced graphene sheets also responsible for the sodium ion storage through scrolling and crumpling process.

In the present work, we obtained highest charge capacity and very low irreversible capacity loss as compared to the literature reports on metal based anodes viz., Sb/C¹⁰ and SnSb/C¹¹. This superior capacity may be due to the Sb particles on flexible rGO sheets assist in the formation of thin SEI layer on its surface due to the irreversible reaction of small amount of Na^+ ions with residual functional groups in rGO for SEI formation hence we observe very low irreversible capacity loss. The coulombic efficiency (Fig. 4b) in the first cycle is 88% but in subsequent cycles it gradually increases and reaches around 93% in the 30th cycle and which stabilizes in subsequent cycles. During alloying

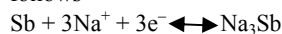
reaction some amount of Na^+ ions are involved in the formation of SEI layer which decreases the coulombic efficiency in the first cycle. In the subsequent cycles during discharging, Na^+ ions may be trapped in between the reduced graphene sheets hence the coulombic efficiency is not so high in subsequent cycles. For real applications the coulombic efficiency should be higher than 99% therefore the material still needs to be improved in the future.

Fig. 4b shows the cycling performance of Sb, rGO and rGO/Sb composites and coulombic efficiency of rGO/Sb composite over the investigated 50 cycles at a current density of 131 mA g^{-1} . The 50th cycle charge capacities are 128, 172 and 598 mAh g^{-1} corresponding to capacity retentions are 21.3, 33.6 and 93% respectively. The poor performance of Sb electrode is due to the volume expansion leading to pulverization of active particles during cycling and results in crumbling of the active particles from the current collector. Though, rGO sheets retain little bit higher capacity retention as compared to Sb anodes, however, restacking is the major issue in the graphene based materials thus results in trapping most of the Na^+ ions inside the sheet folds during prolonged cycling³⁵. However, in the case of rGO/Sb composites, there is no possibility of restacking of rGO sheets and pulverization of active particle during cycling. This is due to the fact that the rGO sheets act as a matrix to hold the Sb particles effectively on its surface during the volume expansion of Sb particles during alloying / dealloying reactions resulting good structural stability and capacity retention. Fig. 4c and 4d presents the charge / discharge curves and cycling performance of rGO/Sb composites at different current densities i.e., from 131 (0.2 C) to 6600 mA g^{-1} (10C). The charge capacities at current densities of 131, 328, 660, 1320, 3300 and 6600 mA g^{-1} are 641, 596, 535, 410, 192 and 100 mAh g^{-1} respectively. Even at a high current density of 6600 mA g^{-1} (10C), we could achieve a charge capacity of 100 mAh g^{-1} . This confirms that the rGO/Sb composite anode material is a suitable candidate for medium drain Na-ion battery applications. Fig. 5a presents the cycling performance of rGO/Sb anode over 150 cycles and the obtained capacity retention of 88% at a current density of 328 mA g^{-1} . The obtained charge capacities and capacity retentions for rGO/Sb composites are superior as compared to Sb/C and SnSb/C composite anodes^{10,11}. Rate capability of the rGO/Sb anodes exhibit superior electrochemical performance as compared to other anodes such as microspheric $\text{Na}_2\text{Ti}_3\text{O}_7$ tiny nanotubes¹², hollow carbon nanowires¹³ and SnO_2 @graphene nanocomposites¹⁴. Fig. 4e presents the cycling performance of rGO/Sb anode over 150 cycles and obtained the capacity retention of 89.5% at the current density of 328 mA g^{-1} .

To confirm the formation of Na_3Sb and know the mechanism of rGO/Sb anode during cycling we have taken TEM images and SAED pattern after first discharge (Fig. 5a), 50 and 150 cycles respectively. The TEM image after first discharge upto 0.01V shows that the formation of Na_3Sb (ICDD reference code: 00-004-0724) alloy on the surface of rGO sheets which is confirmed through SAED pattern. After 50 cycles we observed rGO sheets turn into nanoribbons (Fig. 5b) which hold the active Sb particles tightly on its surface. Further, to confirm the stability of nanoribbons holding the Sb particles, we have taken TEM image and SAED pattern after 150 cycles. It is interesting to note that the well formed nanoribbons (Fig. 5c) firmly hold the active Sb particles. From these observations, we propose the mechanism as

shown in Fig.6 is attributed to the fact that rGO nano ribbons act as a buffer to hold the active Sb particles during alloying reaction which is responsible for good capacity retention over prolonged cycling.

In order to confirm the redox behavior of rGO/Sb composites we carried out the cyclic voltammogram (Fig. 7a) in the potential range 0.01 and 1.5 V at a scan rate of 0.1 mVs⁻¹. The pair of redox peaks observed at 0.78 and 0.41V which is due to the characteristic behavior of Sb anode undergoing alloying / dealloying reaction with Na⁺ ions. This corresponds to the formation of Na₃Sb alloy during cycling. The reaction is as follows



This is one of the very good evidences for the single step alloying reaction of Na⁺ ions with Sb particles. The obtained redox peak pairs of rGO/Sb composites are consistent with the charge / discharge cycling behavior. Further, the CV and charge/discharge cycling experiments confirm that in the composites, Sb particle alone takes part in the electrochemical reaction and rGO strands only act as backbone support to hold the active Sb active particles during electrochemical reaction. Furthermore, this rGO sheets served as conductive media for electron transfer process and maintains a contact between Sb particle and rGO sheets during discharge/charge process^{36, 37}. Thus, rGO sheets act as matrix to hamper the volume expansion of Sb particles during charge / discharge cycling.

Further, to confirm the superior electrochemical performance of rGO/Sb composites, we performed the impedance measurements (Fig. 7b) between 100 KHz to 5 mHz. The inset in Fig. 7b shows the equivalent circuit model for the EIS studies. Sb anode shows the R_{ct} value of 1104 Ω whereas rGO/Sb composite shows only 240 Ω which is nearly four to five times lesser than pure Sb electrodes. Further, we observed the depressed semicircle for rGO/Sb composite which confirms that rGO/Sb composite illustrate higher electronic conductivity as compared to pristine Sb anodes. The sodium ion diffusion coefficients are calculated by using the following formula³⁸

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$

Where T is the absolute temperature, R is the gas constant, n is the number of electrons involved in the electrochemical reaction, A is the surface area, F is the Faraday's number, C is the concentration and D is the diffusion coefficient and σ is the Warburg coefficient which can be obtained from the intersection of the straight line on the real axis³⁹. It is equal to (R_s + R_{ct} - 2σ²C_{dl}). The calculated diffusion coefficient value for Sb and

rGO/Sb composite is 4.18 X 10⁻⁷ and 3.56 X 10⁻⁵ Scm⁻¹ respectively i.e., rGO conductive matrix enhances the diffusion character of Sb electrode by two orders of magnitude. It clearly confirms that rGO conductive matrix enhanced the Na⁺ ion diffusion character of Sb anodes.

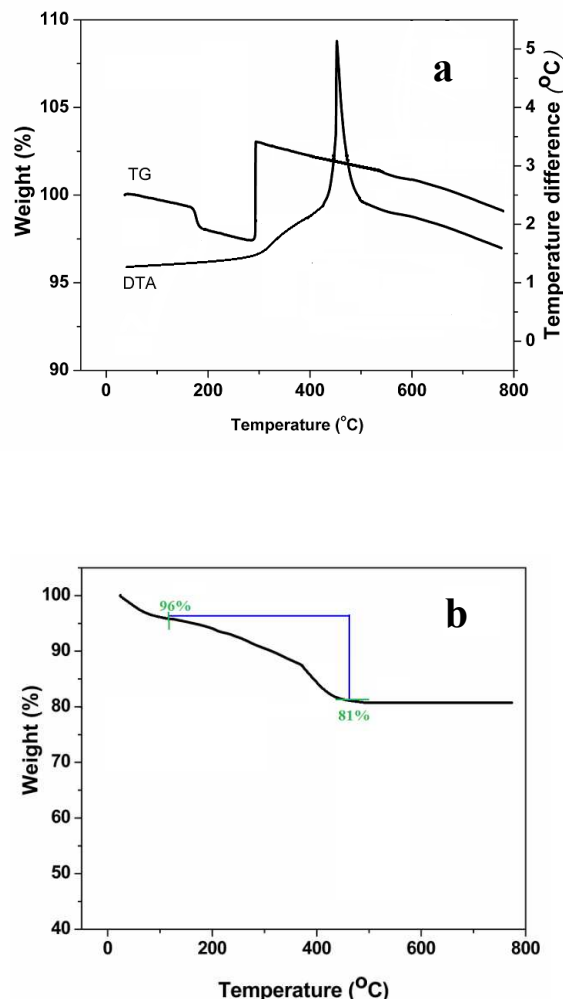


Fig. 1 (a) TG/DTA of bare Sb and (b) TG curve rGO/Sb composite

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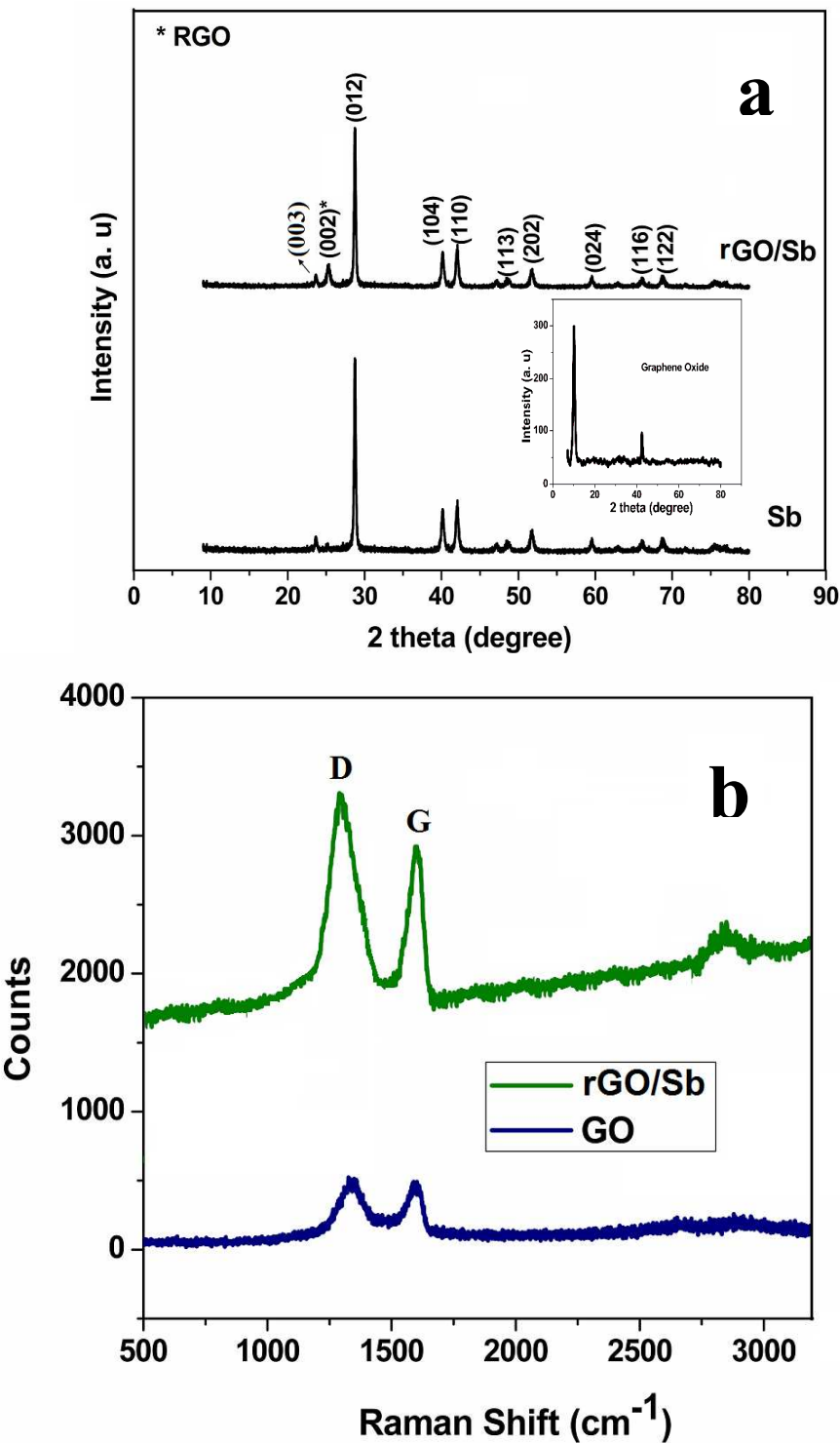


Fig. 2 (a) XRD patterns of Sb and rGO/Sb anode materials. Inset shows XRD pattern of GO. (b) Laser Raman Spectra of GO and rGO/Sb.

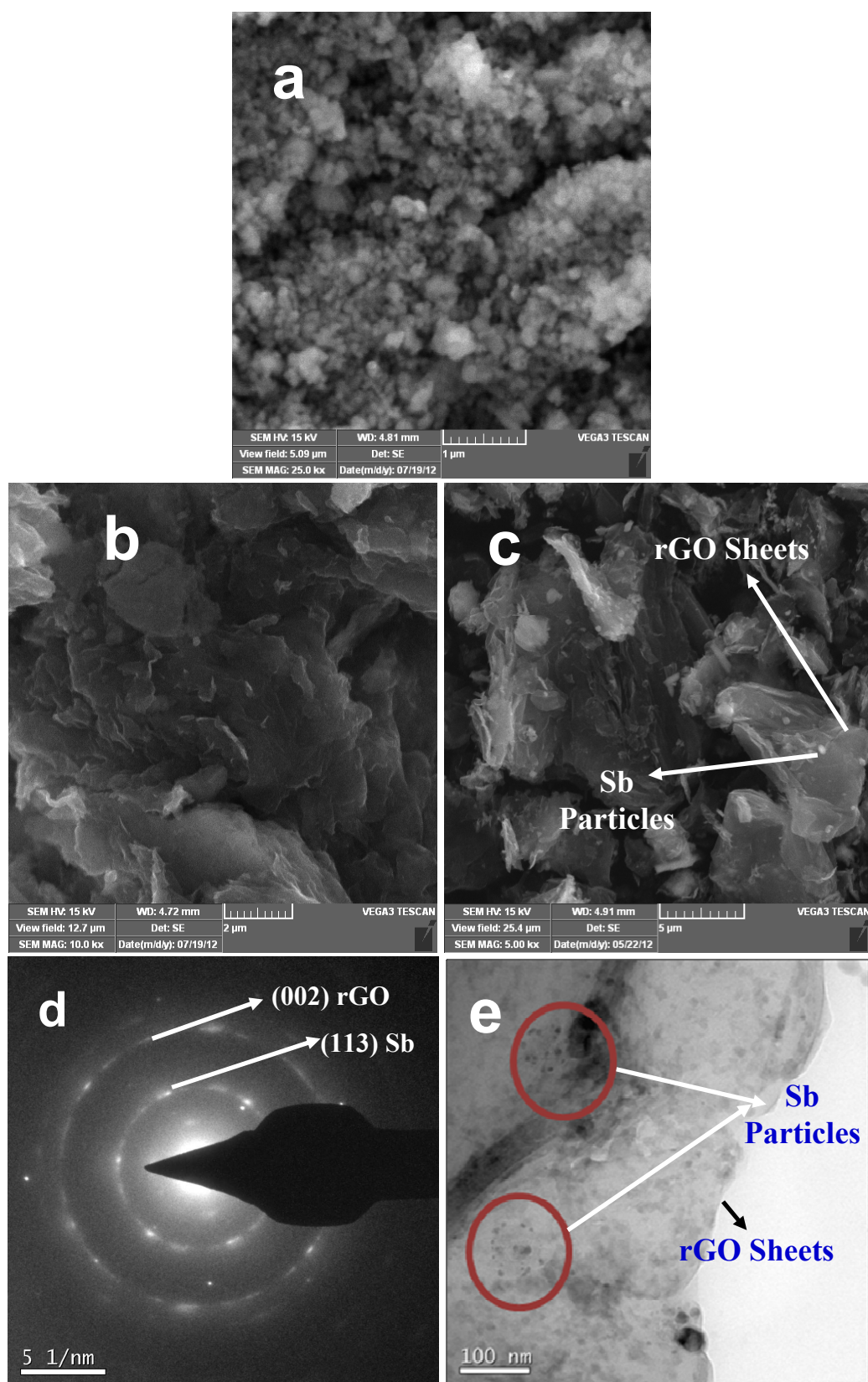


Fig. 3 SEM images of (a) Sb (b) GO (c) rGO/Sb composite (d) SAED pattern of Sb particles in rGO/Sb composite (d) TEM images of rGO/Sb composite.

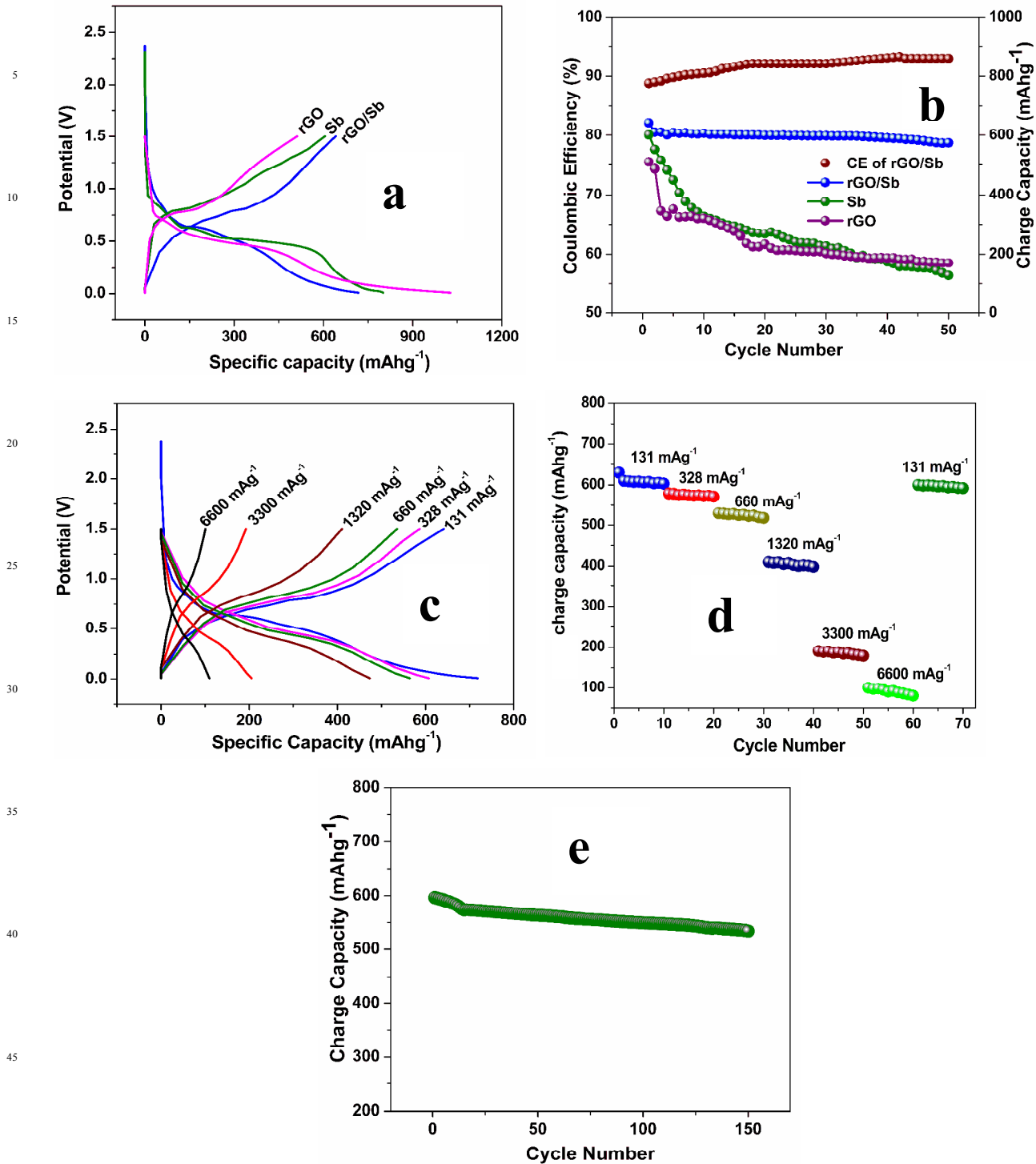


Fig. 4 (a) Charge/discharge curves at a current density of 131 mA g⁻¹ (b) Cycling performance and coulombic efficiency at the current density of 131 mA g⁻¹ (c) Charge/discharge curves of rGO/Sb composite at the different current densities (d) Rate capability of rGO/Sb composite at different current densities (e) Cycling performance of rGO/Sb composite over 150 cycles at the current density of 328 mA g⁻¹.

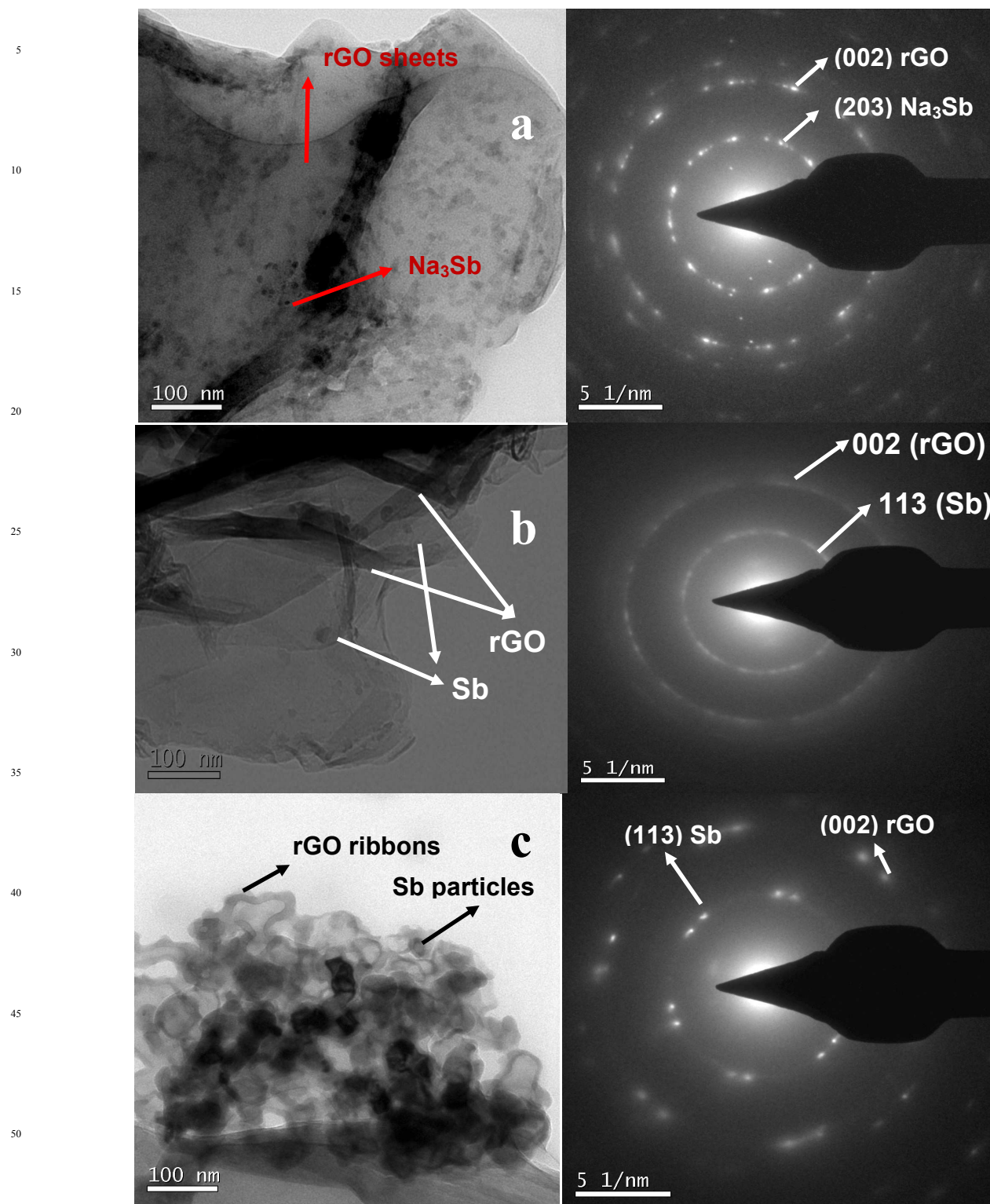


Fig. 5 TEM image and SAED patterns of rGO/Sb composite (a) discharged to 0.01 V (b) after 50 cycles (c) after 150 cycles

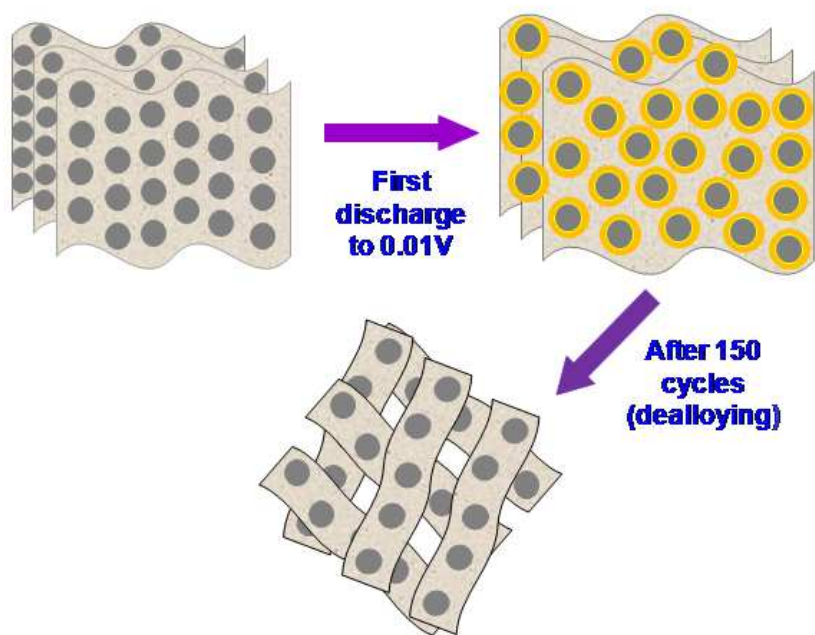


Fig. 6 Mechansim of rGO/Sb composite anode during cycling

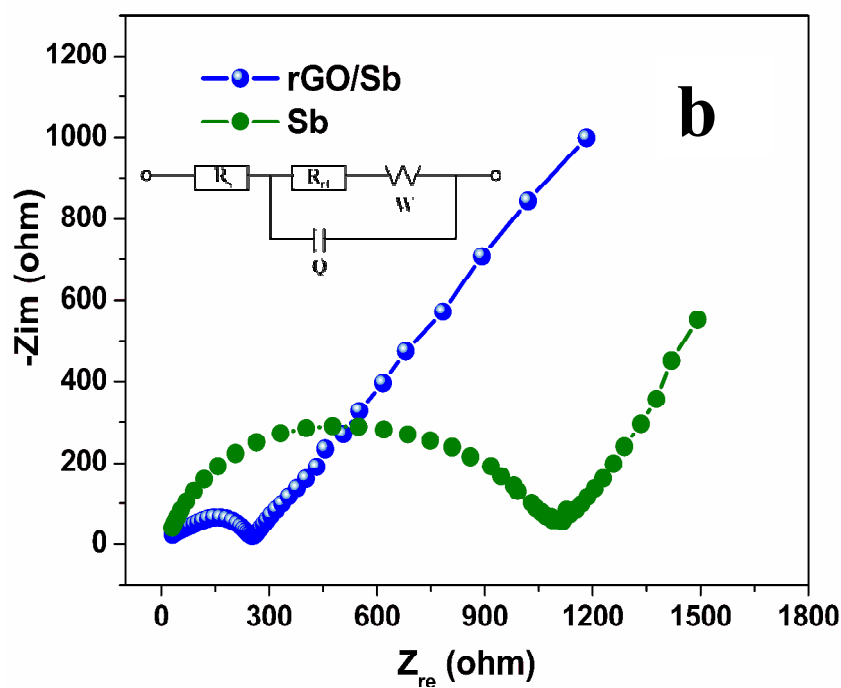
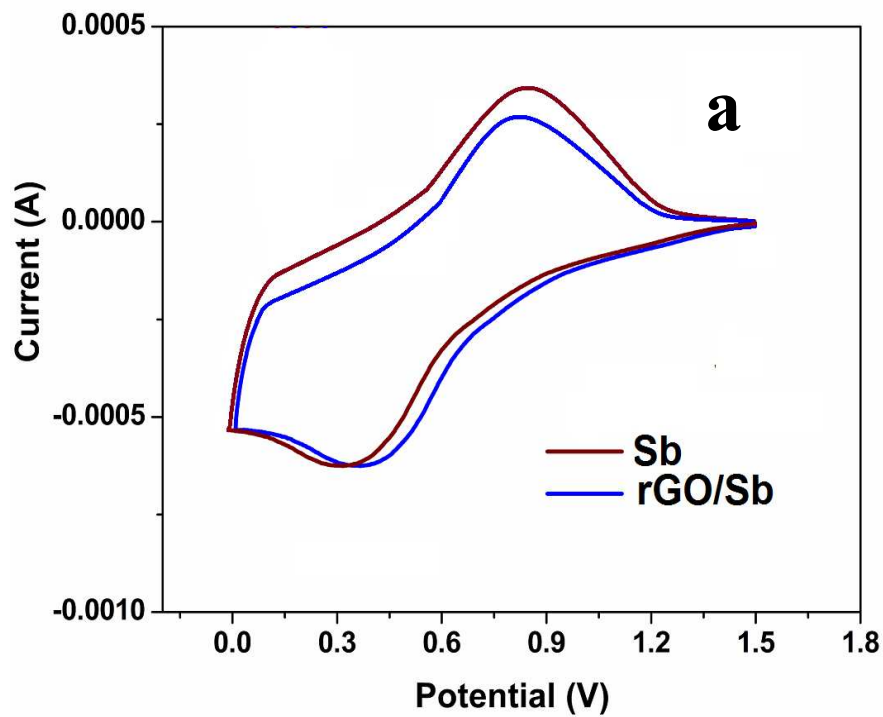


Fig. 7 (a) Cyclic voltammograms of Sb and rGO/Sb composites (b) Nyquist plots of Sb and rGO/Sb composites

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ARTICLE TYPE

Conclusions

In the present work, for the first time we have demonstrated the electrochemical performance of reduced graphene/metal based anodes for sodium ion batteries. The rGO/Sb composite anode delivers the highest charge capacity (641 mAhg⁻¹) with good capacity retention (93%) and also performs well at high rate cycling (>6600 mAg⁻¹). The formation of nanoribbons from rGO nanosheet is responsible for high capacity and capacity retention however; the coulombic efficiency of this material is less than 99% therefore the material still needs to be improved in the future. The results suggest that the rGO/Sb composite is one of the promising anode materials for sodium ion battery applications.

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Notes and references

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1. B. L. Ellis, W. R. M. Makahnouk, Y. Makimura, K. Toghill, L. F. Nazar, *Nat. Mater.* 2007, **6**, 749-753.
2. H. Pan, X. Lu, X. Yu, Y. S. Hu, H. Li, X. Q. Yang, L. Chen, *Adv. Energy Mater.* 2013, **3**, 1186-1194.
3. J. Billaud, G. Singh, R. Armstrong, E. Gonzalo, V. Roddatis, M. Armand, T. Rojo, P. G. Bruce, *Energy Environ. Sci.* 2014, **7**, 1387-1391.
4. H. Pan, Y. S. Hu, L. Chen, *Energy Environ. Sci.* 2013, **6**, 2338-2360.
5. B. Venkata Rami Reddy, S. Gopukumar, *ECS Trans.* 2013, **53**, 49-58.
6. X. Ma, H. Chen, *J. Electrochem. Soc.* 2011, **158**, A1307 – A1312.
7. D. A. Stevens, J. R. Dahn, *J. Electrochem. Soc.* 2000, **147**, 1271-1273.
8. X. Yu, H. Pan, W. Wan, C. Ma, J. Bai, Q. Meng, S. N. Ehrlich, Y. S. Hu, X. Q. Yang, *Nano. Lett.* 2013, **13**, 4721-4727.
9. L. Zhao, H. L. Pan, Y.-S. Hu, H. Li, L. Q. Chen, *Chin. Phys. B* 2012, **21**, 028201-1-4.
10. Y. Wang, X. Yu, J. Bai, R. Xiao, Y. S. Hu, H. Li, X. Q. Yang, L. Chen, X. Huang, *Nat. Commun.* 2013, **4**, 2858.
11. S. Park, I. Gocheva, S. Okada, J. Yamaki, *J. Electrochem. Soc.* 2011, **158**, A1067-A1070.
12. J. Qian, Y. Chen, L. Wu, W. Cao, X. Ai, H. Yang, *Chem. Commun.* 2012, **48**, 7070-7072.
13. L. Xiao, Y. Cao, J. Xiao, W. Wang, L. Kovarik, J. Liu, *Chem. Commun.* 2012, **48**, 3321-3323.
14. W. Wang, C. Yu, Z. Lin, J. Hou, H. Zhu, S. Jiao, *Nanoscale* 2013, **5**, 594-599.
15. D. Su, H. J. Ahn, G. Wang, *Chem. Commun.* 2013, **49**, 3131-3133.
16. Y. Zhang, J. Xie, T. Zhu, G. Cao, X. Zhao, S. Zhang, *J. Power Sources* 2014, **247**, 204-212.
17. L. Zhao, J. Zhao, Y. S. Hu, H. Li, Z. Zhou, M. Aramnd, L. Chen, *Adv. Energy Mater.* 2012, **2**, 962-965.
18. Y. Park, D. Shin, S. H. Woo, N. S. Choi, K. H. Shin, S. Oh, K. T. Lee, S. Y. Hong, *Adv. Mater.* 2012, **24**, 3562-3567.
19. D. Chen, G. Ji, Y. Ma, J. Lee, J. Lu, *Appl. Mater. Interfaces* 2011, **3**, 3078-3083.
20. Y. Zhang, Y.W. Tan, H.L. Stormer, P. Kim, *Nature* 2005, **438**, 201-204.
21. L. Yoo, J. Kim, E. Hosono, H. S. Zhou, T. Kudo, I. Honma, *Nano Lett.* 2008, **8**, 2277-2282.
22. S. Park, R.S. Ruoff, *Nat. Nanotechnol.* 2009, **4**, 217-224.
23. W. S. Hummers, R. E. Offman, *J. Am. Chem. Soc.* 1958, **80**, 1339-1339.
24. X. Zhu, Y. Zhu, S. Murali, M. D. Stoller, R. S. Ruoff, *ACS Nano* 2011, **5**, 3333-3338.
25. T. J. Davies, R. R. Moore, C. E. Banks, R. G. Compton, *J. Electroanal. Chem.* 2004, **574**, 123-152.
26. C. Nithya, S. Gopukumar, *ChemSusChem* 2013, **6**, 898-894.
27. S. Park, J. An, I. Jung, R. D. Piner, S. J. An, X. Li, A. Velamakanni, R. S. Ruoff, *Nano Lett.* 2009, **9**, 1593-1597.
28. J. Zhu, T. Zhu, X. Zhou, Y. Zhang, X. W. Lou, X. Chen, H. Zhang, H. H. Hng, Q. Yan, *Nanoscale* 2011, **3**, 1084-1089.
29. J. Shen, Y. Hu, M. Shi, X. Lu, C. Qin, C. Li, M. Ye, *Chem. Mater.* 2009, **21**, 3514-3520.
30. G. Wang, X. Chen, B. Wang, J. Yao, J. Park, *Carbon* 2009, **47**, 2049-2053.
31. C. N. R. Rao, K. Biswas, K. S. Subrahmanyam, A. Govindaraj, *J. Mater. Chem.* 2009, **19**, 2457.
32. G. Wang, X. Shen, J. Yao, J. Park, *Carbon* 2009, **47**, 2049-2053.
33. J. R. Dahn, T. Zheng, Y. H. Liu, J. S. Xue, *Science* 1995, **270**, 590-593.
34. R. Mukherjee, A. V. Thomas, A. Krishnamurthy, M. Koratkar, *ACS Nano* 2012, **6**, 7867-7878.
35. X. Zhu, Y. Zhu, S. Murali, M. D. Stoller, R. S. Ruoff, *J. Power Sources* 2011, **196**, 6473-6477.
36. A. Yu, H. W. Park, A. Davies, D. C. Higgins, Z. Chen, X. Xiao, *J. Phys. Chem. Lett.* 2011, **2**, 1855-1860.
37. Y. Sun, X. Hu, W. Luo, Y. Huang, *ACS Nano* 2011, **5**, 7100-7107.
38. K. Yang, Z. Deng, J. Suo, *J. Power Sources* 2012, **201**, 274-279.
39. M. Shi, Z. Chen, J. Sun, *Cem. Concr. Res.* 1999, **29**, 1111-1115.