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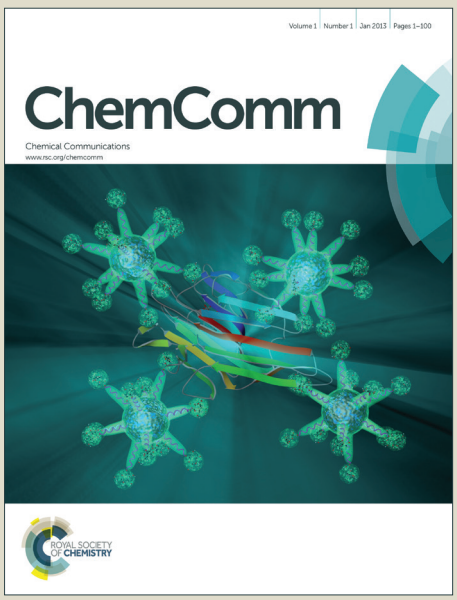

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ARTICLE TYPE

Electrochemical investigation of sodium reactivity with nanostructured Co_3O_4 for sodium-ion batteries

Md Mokhlesur Rahman*, Alexey M. Glushenkov, Thrinathreddy Ramireddy, Ying Chen

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The electrochemical behaviour of Co_3O_4 with sodium is reported here. Upon cycling in the voltage window of 0.01-3.0V, Co_3O_4 undergoes conversion reaction and exhibits a reversible capacity of 447 mAh g^{-1} after 50 cycles. Therefore, nanostructured Co_3O_4 presents feasible electrochemical sodium storage, offering possibilities to develop new anode materials for sodium-ion batteries.

Current interest in Na-ion based batteries arises from the potential of these devices to become less expensive, safer and environmentally benign with respect to present Li-ion technologies. In a world with a growing concern about energy management issues, sodium has strongly broken into energy storage research field. This alkali holds promise for being a complement or substituting Li-based technology.[1] Its natural abundance, easy access to sodium sources and, consequently, lower price; suitable redox potential (-2.71 V, vs. standard hydrogen electrode) and similar intercalation chemistry to Li, make this element strategic in innovative research of energy storage systems. [1-3] However, the radius of sodium ions (1.06 Å) is obviously larger than that of lithium ions (0.76 Å), which makes it more difficult to identify electrode materials for Na-ion batteries.[4] Therefore, in order to make sodium-ion batteries viable, identification of suitable anode and cathode materials is critical. Even though, a variety of sodium host cathodes have been reported to have certain Na-storage capacity and cycleability, [5-9] but the anodic host have been less successfully developed.

Just as lithium counterparts, the anode materials for sodium-ion batteries are expected to operate via a range of similar mechanisms, e.g. intercalation, alloying-dealloying and conversion reactions. It has been demonstrated, however, that many materials considered as promising anode materials for lithium-ion batteries do not work at all or demonstrate only a limited redox electrochemical activity in sodium-ion batteries. For example, graphite, the most used commercial anode material in lithium-ion batteries can intercalate virtually no sodium and, consequently, is not a prospective anode for sodium-ion batteries.[3] Two other popular large capacity anode materials for lithium-ion batteries, silicon and germanium, have no detectable redox electrochemical activity in sodium-ion batteries.[10] Some other materials, e.g. hard carbons, are electrochemically active in Na-ion batteries while their reactivity with lithium is very limited.[3, 11-13] On the contrary, many metal oxides are well known for lithium storage but still remain unexplored for analogous sodium storage.

Until now, only a few studies have reported the sodium storage properties of metal oxides, including Fe_3O_4 and α-Fe_2O_3,[14] Sb_2O_4 thin film,[15] TiO_2 nanotubes,[16] $NiCo_2O_4$,[17] α-MoO_3,[18] and SnO_2.[19] These works provide some information on sodium electrochemistry of metal oxides and their possibility to use as anodes for the development of sodium-ion batteries. Here we attempted to extend the electrochemical investigation of cobalt oxide (Co_3O_4) with sodium. In this study, we have demonstrated a possible conversion reaction of Co_3O_4 with sodium with a reversible capacity of 447 mAh g^{-1} and ~ 86 % capacity retention after 50 cycles.

The Co_3O_4 powder was synthesized by single step molten salt precipitation process (for experimental details, see ESI). The XRD pattern of the Co_3O_4 powder is shown in Fig. 1a. All diffraction peaks are consistent with the cubic phase of Co_3O_4 [JCPDS no. 00-043-1003, space group *Fd-3m* (no. 227)]. No peaks of any other phases or impurities were detected, demonstrating that materials with high purity could be obtained using the present synthesis strategy. The diffraction peaks at 19.0, 31.2, 36.8, 44.8, 59.3 and 65.2° are associated with the 111, 220, 311, 400, 511, and 440 reflections of Co_3O_4, indicating successful synthesis of Co_3O_4. Fig. 1b shows SEM image of the Co_3O_4 powder. It is found that Co_3O_4 sample consists of agglomerated clusters of nanoparticles with a pyramid like morphology (inset of Fig1b). More SEM images are shown in Fig. S1 (ESI), which further depicts the morphological features of Co_3O_4 sample.

To obtain information concerning structural and morphological evolution of the sample, TEM measurements were carried out. Bright-field imaging of the sample reveals dense agglomerates of fine (<10 nm) and much coarser (> 30 nm) crystalline Co_3O_4 (Fig. 2a and Fig. S2 (ESI)). The corresponding selected area electron diffraction (SAED) pattern is depicted in Fig. 2b. The SAED pattern consists of single component of Co_3O_4 with a *d* spacing of 0.476, 0.288, 0.242, 0.211, and 0.156 nm which can be referred to the crystallographic directions of (111), (220), (311), (400), and (511), respectively. This result is consistent with the XRD pattern obtained for this sample as shown in Fig.1a. A HRTEM image is shown in Fig. 2c. The marked *d*-spacing of 0.291 nm corresponding well with that of (220) planes of cubic Co_3O_4.

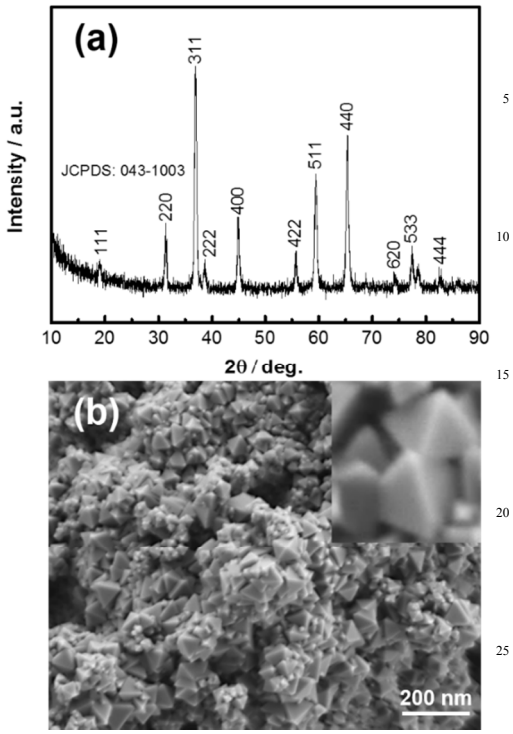

Fig. 1 (a) XRD pattern and (b) SEM image of Co_3O_4 sample.

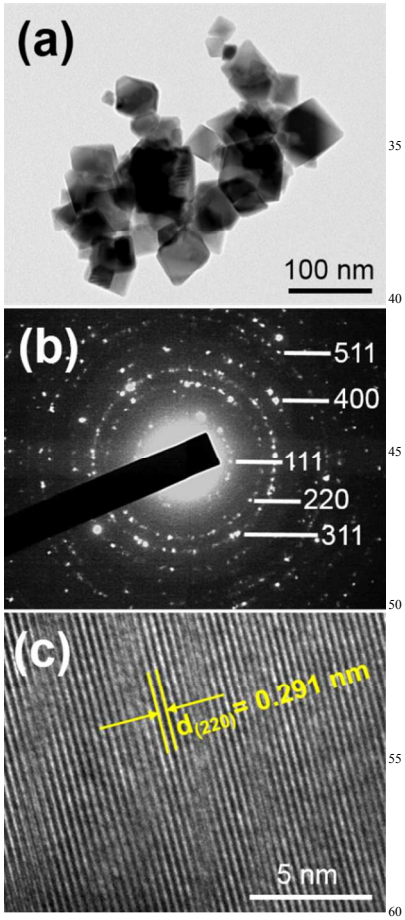

Fig. 2 TEM images of Co_3O_4 sample: (a) a bright-field image; (b) corresponding SAED pattern; and (c) HRTEM image of Co_3O_4 crystal with a *d* spacing of 0.291 nm corresponding well with that of (220) planes.

The electrochemical performance of the Co_3O_4 electrodes was evaluated using CR 2032 coin-type cells in which Na metal was used as the counter/reference electrode (for experimental details, see ESI). The cells were galvanostatically discharged-charged in the voltage range of 0.01-3.0 V. Fig. 3a shows the cycling performance of Co_3O_4 electrode at a current density of 25 mA g^{-1}. The measured 1st and 50th cycle discharge/charge capacities were 520/245 and 447/446 mAh g^{-1} with a Coulombic efficiency of ~ 47 % for the 1st and ~ 100 % for the 50th cycle, respectively. At the 50th cycle, the Co_3O_4 electrode delivered a reversible capacity of 447 mAh g^{-1}, which is ~ 86% of the initial discharge capacity. Fig. 3b presents the discharge-charge voltage profiles for the 1st, 2nd, 15th, 25th, and 50th cycle at a current density of 25 mA g^{-1}. The first discharge curve displayed all the characteristic features related to the various stages of sodiation. The first discharge profile exhibits a plateau around 0.8V (SEI layer formation) and a bump around 0.6 V, followed by a long tail at a lower voltage. The features of the first discharge curve confirm that conversion process is existing for the sodiation of Co_3O_4 electrode. However, the SEI layer formation voltage of Co_3O_4 electrode is different between Na-ion and Li-ion system. Na/Na^+ system shows lower SEI layer formation voltage (~ 0.8V) than that of Li/Li^+ system (above 0.8V) and SEI layer formation plateau for Na/Na^+ system is not as sharp/long as Li-ion cell.[20, 21] On the other hand, the initial sodiation capacity of Co_3O_4 electrode is much lower than Li-ion cell.[20, 21] Therefore, these two points are reinforcing the idea that a full conversion could not occur in this sodiation process initially. The voltage platform of the charge curves upon de-sodiation were quite similar to those of de-lithiation. Only difference is the process of Na^+ release at a lower voltage of ~1.5V compared to that of Li^+ (~2.1V).

To further assess the electrochemical reactivity of Co_3O_4 with Na, cyclic voltammetry studies were performed at a scan rate of 0.05 mV s^{-1} in the voltage range of 0.01-3.0V (Fig. 3c). The first cycle reduction (cathodic scan) results in a broad peak centred at ~0.5V with a small peak at 0.75 V. This reduction process is corresponding to the partial reduction of Co_3O_4 to metallic cobalt (Co), the electrochemical formation of Na_2O, and the formation of a partially irreversible solid electrolyte interphase (SEI) layer. The broad feature of this reduction peak is also consistent with the partial conversion process initially. A full conversion process gives a very strong sharp peak in the first reduction process for the Li-ion cell. [22, 23] In the subsequent cycles, only one cathodic peak can be observed at around 0.54V. However, peaks are positively shifted to a higher voltage with respect to the first cycle, which is ascribed to the polarisation effect of the electrode in the first cycle.[24] In the oxidation process (anodic scan), there is a peak at 1.5V, corresponds to the re-oxidised of Co to Co_3O_4 and Na_2O decomposes. Theoretically, the formation of Co and Na_2O and the re-formation of Co_3O_4 can be described by the following electrochemical conversion reaction:

$$Co_3O_4 + 8Na^+ + 8e^- \leftrightarrow 4Na_2O + 3Co \quad (1)$$

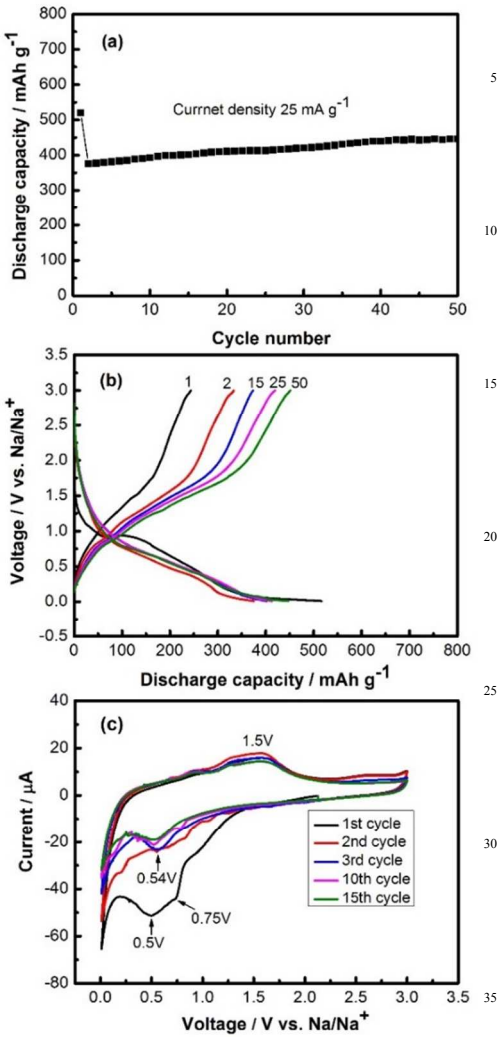

Fig. 3 Electrochemical performance of Co_3O_4 electrodes at 0.01-3.0 V (vs. Na/Na^+): (a) cycling performance at a current density of 25 mA g^{-1}; (b) corresponding galvanostatic discharge-charge voltage profiles for the 1st, 2nd, 15th, 25th , and 50th cycle; and (c) cyclic voltammogram recorded at a scan rate of 0.05 mV s^{-1} between 0.01 and 3.0V.

In order to determine the Na-storage mechanism in Co_3O_4, *ex situ* XRD measurements were performed on electrodes after cycling (Fig. 4). Fig. 4a shows *ex situ* XRD patterns of the fully discharged-charged electrodes for the first cycle. First cycle discharge to 0.01V, XRD pattern demonstrates that all diffraction peaks are well indexed to the cubic Co_3O_4 phase (JCPDS no. 00-043-1003) with a small unknown peak at around 32.7°. First cycle charge back to 3.0V, *ex situ* XRD pattern confirms the existence of Co_3O_4 phase. To get further information, we selected the 20th cycle fully discharged-charged electrode for *ex situ* XRD measurements (Fig. 4 b). Surprisingly, all diffraction peaks for the Co_3O_4 phase tend to disappear and a new phase of Na_2O (JCPDS no. 00-003-1074) appears when electrode was discharged to 0.01V. At the same time there should also have evidence of Co (JCPDS no. 00-015-0806) phase formation. Unfortunately there is significant overlap of this peak with copper current collector peak in the measured XRD patterns. On the other hand, when electrode was charged back to 3.0V, all diffraction peaks for the Co_3O_4 phase appear. These findings suggest that the conversion reaction is not completed in the first discharge to 0.01V, thus the Co_3O_4 phase still exists in the first discharge and visible again when charge back to 3.0V. The conversion reaction tends to take place fully with increasing cycling number. It is anticipated that discharge capacity will keep increasing until all materials get involved in the conversion reaction and then capacity will keep constant or may decline.

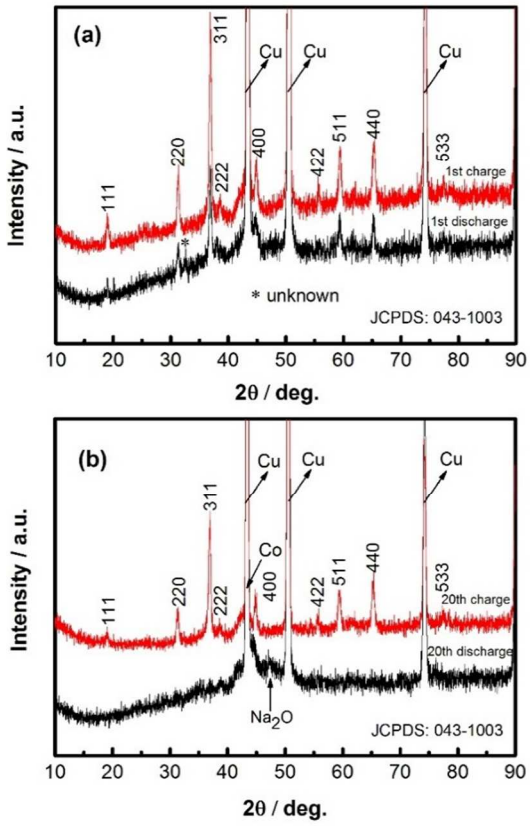

Fig. 4 *ex-situ* XRD patterns of Co_3O_4 electrodes: (a) First cycle fully discharged-charged state; (b) 20th cycle fully discharged-charged state.

In conclusion, low temperature molten salt synthesis of nanostructured Co_3O_4 with a bimodal size distribution of particles, very fine (< 10 nm) and coarser (> 30 nm) has successfully been achieved. The electrochemical sodiation/de-sodiation of nanostructured Co_3O_4 was reversible over an extended voltage range of 0.01-3.0 V vs. Na/Na^+. Overall, these preliminary results indicate that Co_3O_4 could be used as a possible negative electrode for more sustainable cost-effective Na-ion batteries. Discharging Co_3O_4 at a lower voltage of 0.01V vs. Na/Na^+ offers a characteristic voltage profile for oxide conversion similar to that occurring upon lithiation of Co_3O_4, however, sodiation was not as pronounced as that caused by lithiation. This was likely due to the larger size of the Na^+ ions and their reduced mobility. Charging back to 3.0V vs. Na/Na^+ upon de-sodiation was quite similar to those of de-lithiation. The

reversible capacity as high as 447 mAh g^{-1} was attained after 50 cycles at 25 mA g^{-1} current, being this value still comparable with those of other state-of-the-art materials for Na-ion batteries. Moreover, the obtained result is undoubtedly helpful to further advance towards sodium electrochemistry of nanostructured Co_3O_4.

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Notes and references

Institute for Frontier Materials, Deakin University, Waurn Ponds, VIC 3216, Australia.
Fax:+ 61352271103; Phone:+61352272642
E-mail: m.rahman@deakin.edu.au

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1 V. Palomares, M. Casas-Cabanas, E. Castillo-Mart´ınez, M. H. Han, T. Rojo, *Energy Environ. Sci.*, 2013, **6**, 2312.
2 J. Qian, Y. Chen, L. Wu, Y. Cao, X. Ai, H. Yang, *Chem. Commun*., 2012, **48**, 7070.
3 S. W. Kim, D.H. Seo, X.H. Ma, C. Ceder, K. Kang, *Adv. Energy Mater.*, 2012, **2**, 710.
4 M. D. Slater, D. Kim, E. Lee, C. S. Johnson, *Adv. Funct. Mater*., 2013, **23**, 947.
5 Y. Cao, L. Xiao, W. Wang, D. Choi, Z. Nie, J. Yu, L. V. Saraf, Z. Yang, J. Liu, *Adv. Mater.*, 2011, **23**, 3155.
6 R. Berthelot, D. Carlier, C. Delmas, *Nat. Mater*., 2011, **10**, 74.
7 J. Qian, M. Zhou, Y. Cao, X. Ai, H. Yang, *Adv. Energy Mater*., 2012, **2**, 410.
8 M. Zhou, L. Zhu, Y. Cao, R. Zhao, J. Qian, X. Ai, H. Yang, *RSC Advances*, 2012, **2**, 5495.
9 R. Zhao, L. Zhu, Y. Cao, X. Ai, H. X. Yang, *Electrochem. Commun*., 2012, **21**, 36.
10 V. L. Chevrier, G. Ceder, *J. Electrochem. Soc.*, 2011, **158**, A1011.
11 V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-Gonzalez, T. Rojo, *Energy Environ. Sci.*, 2012, **5**, 5884.
12 M.D. Slater, D. Kim, E. Lee, C.S. Johnson, *Adv. Funct. Mater.*, 2013, **23**, 947.
13 B.L. Ellis, L.F. Nazar, *Solid State and Materials Science*, 2012, **16**, 168.
14 S. Komaba, T. Mikumo, N. Yabuuchi, A. Ogata, H. Yoshida, Y. Yamada, *J. Electrochem. Soc.,* 2010, **157**, A60.
15 Q. Sun, Q.Q. Ren, H. Li, Z.W. Fu, *Electrochem. Commun*., 2011, **13**, 1462.
16 H. Xiong, M.D. Slater, M. Balasubramanian, C.S. Johnson, T. Rajh, *J. Phys. Chem. Lett.*, 2011, **2**, 2560.
17 R. Alcantara, M. Jaraba, P. Lavela, J.L. Tirado, *Chem. Mater.*, 2002, **14**, 2847.
18 S. Hariharan, K. Saravanan, P. Balaya, *Electrochem. Commun.*, 2013, **31**, 5.
19 Y. Wang, D. Su, C. Wang, G. Wang, *Electrochem. Commun*., 2013, **29**, 8.
20 X. Guo, W. Xu, S. Li, Y. Liu, M. Li, X. Qu, C. Mao, X. Cui, C. Chen, *Nanotechnology*, 2012, **23**, 465401.
21 X. Yang, K. Fan, Y. Zhu, J. Shen, X. Jiang, P. Zhao, C. Li, *J. Mater. Chem.,* 2012, **22**, 17278.
22 M.M. Rahman, J.Z. Wang, X. L. Deng, Y. Li, H. K. Liu, *Electrochim. Acta*, 2009, **55**, 504.
23 Y. Yao, J. Zhang, T. Huang, H. Mao, A. Yu, *Int. J. Electrochem. Sci*., 2013, **8**, 3302.
24 X. Yang, K. Fan, Y. Zhu, J. Shen, X. Jiang, P. Zhao, C. Li, *J. Mater. Chem*., 2012, **22**, 17278.