Three-dimensionally scaffolded Co₃O₄ nanosheet anodes with high rate performance

Jinyun Liu,^{a,b} Sean J. Kelly,^b Eric S. Epstein,^b Zeng Pan,^b Xingjiu Huang,^a Jinhui Liu,^a Paul V. Braun^{b,*}

^a Research Center for Biomimetic Functional Materials and Sensing Devices, Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, Anhui 230031, PR China

^b Department of Materials Science and Engineering, Frederick Seitz Materials Research Laboratory, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

* Corresponding author: pbraun@illinois.edu

Tel.: 1-217-244-7293; Fax: 1-217-333-2736

Abstract:

Advances in secondary batteries are required for realization of many technologies. In particular, there remains a need for stable higher energy batteries. Here we suggest a new anode concept consisting of an ultrathin Co_3O_4 nanosheet-coated Ni inverse opal which provides high charge-discharge rate performance using a material system with potential for high energy densities. Via a hydrothermal process, about 4 nm thick Co_3O_4 nanosheets were grown throughout a three-dimensional Ni scaffold. This architecture provides efficient pathways for both lithium and electron transfer, enabling high charge-discharge rate performance. The scaffold also accommodates volume changes during cycling, which serves to reduce capacity fade. Because the scaffold has a low electrical resistance, and is three-dimensionally porous, it enables most of the electrochemically active nanomaterials to take part in lithiation-delithiation reactions, resulting in a near-theoretical capacity. On a Co_3O_4 basis, the $\text{Ni}@\text{Co}_3\text{O}_4$ electrode possesses a capacity of about 726 mAh g^{-1} at a current density of 500 mA g^{-1} after 50 cycles, which is about twice the theoretical capacity of graphite. The capacity is 487 mAh g^{-1} , even at a current density of 1786 mA g^{-1} .

Keywords: Mesostructured electrode; anode; secondary battery; high power; nanostructure

1. Introduction

Lithium-ion secondary batteries have found broad application since first commercialized in the early 1990s by Sony [1], and are now being used for applications ranging from consumer electronics to electric vehicles and electrical grid storage [2–4]. Typically, graphite is used as an anode in Li-ion secondary batteries due to its attractive properties which include its low-cost, ease of processing, and good conductivity [5, 6]. However, graphite possesses a theoretical capacity of 372 mAh g^{-1} , which limits the available energy density of commercial batteries. Graphite also presents a number of safety issues. The low lithium intercalation voltage at the graphite electrode can lead to lithium plating during cycling, which can cause fires and explosions [7]. This issue is particularly important during fast charging. Over the past decade, considerable efforts have been made to develop alternative electrodes with improved electrochemical performance [8–12]. Nanostructuring has been receiving attention for enhancing electrode performance, in particular due to the potential for providing electrodes with high surface areas and short electron and ion transport pathways. However, high surface areas may also lead to undesirable side reactions, which must be considered.

Since Tarascon first reported the use of a nanoscale transition metal oxide as an anode material [13], many transition metal oxides anodes have been considered [14, 15]. Co_3O_4 is considered promising due to its high theoretical capacity of 890 mAh g^{-1} [16–20], which has led to a number of reports on the fabrication of Co_3O_4 -based anodes, including approaches based on redox precipitation [21], H_2O_2 -controlled hydrothermal processes [22], solvothermal [23] and molten salt [24] methods, and the electrochemical properties of nanostructured Co_3O_4 [25–29]. The electrical conductivity of Co_3O_4 is poor, and thus to form an anode which

can be cycled at an appreciable rate, Co_3O_4 is usually mixed with an electrically conductive phase. Co_3O_4 -graphene composite structures have been of particular interest due to the excellent conductivity of graphene, and the two-dimensional (2D) nature of graphene, which provides a high contact area to Co_3O_4 [30–32]. For transition metal oxide systems in general, providing efficient pathways for electrons, is of particular importance, given the poor conductivities of both most transition metal oxides, and Li_2O , the product of the reaction with lithium. It is also important to avoid aggregation of the electrochemically active phase during the charge-discharge process and to accommodate any volume changes during cycling.

Here we present an ultrathin nanosheet-coated three-dimensional (3D) inverse opal anode, fabricated as outlined in Scheme 1. The Ni inverse opal scaffold was fabricated by electrodeposition of Ni metal through a sacrificial polystyrene opal template following our previous procedures [33, 34]. Ultrathin Co_3O_4 nanosheets (4 nm thick) were hydrothermally grown onto the Ni scaffold followed by a heat treatment. As fabricated, the electrode provides a very short pathway for lithium and electrons in the Co_3O_4 , is mechanically stable, and provides good long-range electrical conductivity. Because the Co_3O_4 is attached to the surface of the porous 3D inverse opal, Co_3O_4 aggregation can be avoided, enabling most of the active nanomaterials to take part in the electrochemical reactions during the charge-discharge process.

2. Experimental

2.1. Ni inverse opal fabrication

The Ni inverse opal fabrication is similar to our previous reports [35, 36] with some

modifications. Typically, glass substrates were first cleaned with piranha solution (volume ratio of H_2SO_4 to H_2O_2 is 3:1; Caution, piranha is highly corrosive and potentially explosive) and coated with ~5 nm Cr and ~60 nm Au by e-beam evaporation (Temescal, Inc). To modify the surface of the substrate for polystyrene opal growth, the gold-coated substrate was immersed in a 0.5 mM aqueous solution of 3-mercapto-1-propanesulfonic acid, sodium salt (Sigma-Aldrich Corp.) for 2 h. Polystyrene spheres with a diameter of 600 nm (Molecular Probes) were dispersed in Millipore water to prepare a 0.2 wt% suspension. After drying, the pre-treated substrate was placed vertically in a vial with the polystyrene suspension at 55 °C for deposition (Supplementary Information Fig. S1a). The resulting polystyrene opal was sintered at 95 °C for 3 h to increase the pore size of the electroplated Ni inverse opal. The Ni inverse opal was electrodeposited using current of 2 mA cm^{-2} in a commercial electroplating solution (Techni Nickel S, Technic Corp.), to an approximate size of 2 cm x 1 cm x 8 μm , as described in Fig. S1b. The sample was immersed in toluene (Sigma-Aldrich Corp.) to remove the polystyrene template. The resulting Ni inverse opal was rinsed alternately with ethanol and Millipore water, and dried in an oven at ~60 °C.

2.2. Co_3O_4 nanosheet growth

Ultrathin Co_3O_4 nanosheets were grown on the Ni inverse opal via a hydrothermal process followed by a heat treatment, similar to previous report [37] with some modifications optimized for our study at here. 1 mmol of $\text{Co}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, 2 mmol of NH_4F , and 4 mmol of urea ($\text{CO}(\text{NH}_2)_2$) were dissolved into 40 mL of Millipore water under stirring for 15 min. This solution was transferred into a 50 mL Teflon-lined steel autoclave. A $1 \times 2 \text{ cm}^2$ Ni inverse opal

coated substrate was inserted into the solution Ni face up. The autoclave was sealed and heated in an oven at 110 °C for 6 h. The oven was turned off and allowed to naturally cool to room temperature. The substrate was removed from the autoclave, thoroughly washed with ethanol and Millipore water and dried in air at 50 °C for 2 h. The sample was then heat treated in a tube furnace at 400 °C for 1.5 h under ultrahigh purity Ar gas to crystallize Co₃O₄ (Ar was used to minimize oxidization of Ni scaffold. The ramp rate was 5 °C min⁻¹. The furnace was then turned off and allowed to cool naturally.

Ni inverse opals coated with thick Co₃O₄ nanosheets and a Co₃O₄ thin film on Ni film substrate were also prepared for comparison of the electrochemical properties. A solution containing 5 mmol of Co(NO₃)₃·4H₂O, 6 mmol of NH₄F, and 10 mmol of CO(NH₂)₂ in 40 mL of Millipore water was used to prepare the thick Co₃O₄ nanosheets for coating onto Ni inverse opal. Other procedures were the same as in the preparation of thin Co₃O₄ nanosheets. For the preparation of a Co₃O₄ thin film on Ni film substrate, electrodeposition of Ni was performed on a gold-coated glass substrate (no opal). Then, the Co₃O₄ film was grown on the Ni film through the same procedure as that used for preparing the Ni@ultrathin Co₃O₄ nanosheet inverse opal electrode.

2.3. Characterization

XRD was collected using a Philips X'pert MRD X-ray diffractometer (XRD) with Cu K α radiation (1.5418 Å). Diffraction patterns were recorded at room temperature over the 2 θ range of 10 to 80°. The XRD peaks were compared with Joint Committee on Powder Diffraction Standards (JCPDS). The morphology, structure and composition of the samples

were investigated using a Hitachi S-4800 scanning electronic microscope (SEM), a Hitachi S-4700 SEM equipped with an Oxford INCA energy dispersive X-ray (EDX) analyzer, and a JEOL 2100 Cryo transmission electron microscope (TEM) operating at 200 kV. Elemental mappings were carried out on the Hitachi S-4700 SEM. Active material loading was determined *via* inductively coupled plasma (ICP) analysis using a PerkinElmer Elan DRCE ICP-MS.

2.4. Electrochemical measurements

Electrochemical tests were performed using two-electrode cells with lithium metal as the counter and reference electrodes using Princeton Applied Research Model 273A and Biologic VMP3 potentiostats. The Co_3O_4 -coated structures were set as the working electrodes. Cell assembly was performed in an Ar-filled glove box. A non-aqueous electrolyte consisting of 1 M of LiClO_4 into a 1: 1 mass ratio mixture of ethylene carbonate and dimethylene carbonate was used. The electrode capacities were measured by a galvanostatic charge-discharge method at a current density of 500 mA g^{-1} (0.56C, a rate of 1C corresponds to complete charge or discharge of theoretical capacity in one hour) over the potential range of 5 mV to 3.0 V. Cyclic voltammetry (CV) data were recorded over the potential range of 0.0 to 3.0 V at a scan rate of 0.1 mV s^{-1} .

3. Results and discussion

The electrode morphologies at various stages of the fabrication process are shown in Fig. 1. In Fig. 1a, it can be seen that the polystyrene spheres self-assemble into an ordered opal

structure (cross section shown in Fig. S2a). The slightly merged sphere contact points after the 95 °C treatment result in a more porous Ni inverse opal structure after template removal (Fig. 1b). Low-magnification top-view and cross section SEM images are shown in Fig. S2b and c, respectively. The Ni inverse opal exhibits an interconnect window pore diameter of about 80 nm between adjacent cavities. We have generally found an enlarged interconnect is important for ion diffusion through the structure to obtain uniform Co_3O_4 deposition through the thickness of the inverse opal during the hydrothermal growth. Small pores substantially limit ion diffusion, diminishing the growth of materials at the bottom of inverse opal. Fig. 1c-f show the top and cross-sectional SEM images of the Ni scaffold coated with the Co_3O_4 nanosheets (after the heat treatment) at both lower- and higher-magnification. The uniformity of Co_3O_4 deposition in each cavity indicates that the ultrathin Co_3O_4 nanosheets grew throughout the whole inverse opal, including the bottom (Fig. S2d).

Via glancing angle XRD (Fig. 2) a weak and broad diffraction peak centered at 18.6° is observed, which correlates with the (111) plane of cubic phase Co_3O_4 (JCPDS card No. 42–1467). Under a normal scan mode from 10° to 80° 2θ (Fig. 2, inset), the Co_3O_4 peak is barely observed. The peaks at 38.1° , 44.7° , and 52.2° can be indexed to Au (111), Ni (111), and Ni (200) from the substrate and the scaffold. There was no sign of NiO or other impurities in either the glancing angle or conventional XRD.

The structure of the ultrathin Co_3O_4 nanosheets removed from a $\text{Ni}@\text{Co}_3\text{O}_4$ inverse opal via ultrasonication in ethanol for 1 h was investigated in depth by TEM (Fig. 3). From Fig. 3c, and Fig. S3, the nanosheet thickness is found to be about 4 nm. Lattice fringes with spacings of 0.47 and 0.28 nm, corresponding to the (111) and (220) planes of cubic Co_3O_4 , respectively

can be observed. Selected area electron diffraction (SAED) (Fig. 3d) indicates the Co_3O_4 is polycrystalline.

The nanosheet morphology is consistent with SEM observations. ~2 to 4 nm mesopores can be observed in the higher magnification TEM image (Fig. 3b). The mesopores are distributed through the nanosheets at high densities. We suspect a high density of pores is valuable to enable lithium ions to diffuse through the electrode (otherwise ion diffusion would likely be blocked). We do not know the mechanism for formation of the pores in the nanosheets, but perhaps they form during the heat treatment as the hydrothermally deposited phase densifies and crystalizes. The pores may also provide additional free space to accommodate the volume expansion of Co_3O_4 along the lateral direction. As we previously showed for a silicon coated Ni inverse opal anode [33], the 3D porous Ni inverse opal is compatible with systems which undergo rather large volume expansions.

To determine the distribution and loading of the Co_3O_4 nanosheets through the Ni inverse opal, both elemental mappings and ICP measurements were performed. As can be seen from the elemental mapping (Fig. 4), Co is uniformly distributed throughout the Ni inverse opal, indicating that the Co_3O_4 nanosheets grew throughout the Ni inverse opal. By ICP, the Co to Ni atomic ratio is 0.15, giving a mass fraction of Co_3O_4 in the electrode, including the Ni current collector, of 19.4wt%, which corresponds to a loading ~0.71 mg in the 2 cm^2 , 8 μm thick electrode. We recognize the filling fraction of Co_3O_4 in the electrode is not high, which will reduce the energy density of the electrode, and for application it needs to be increased. We suspect the Co_3O_4 loading of the electrode can be increased by electropolishing the Ni scaffold, as we previously demonstrated [36], using a lower density scaffold (*e.g.*

carbon-based) [38–40], or by increasing the surface area of the structure by reducing the colloid diameter. We intend to investigate these strategies in the future.

CV curves of the Ni@Co₃O₄ nanosheet inverse opal anode are shown in Fig. 5a. The reactions between Co₃O₄ and Li-ions during charging and discharging are expressed in Equations 1 and 2 [41–43]. In the first cathodic process, a sharp peak at about 0.85 V can be ascribed to the reduction of Co₃O₄ into CoO. The relatively broad peak around 0.55 V can be attributed to both reduction of CoO to Co and solid electrolyte interface (SEI) formation. Moreover, a weak peak at about 0.1 V could be caused by the reversible formation-dissolution of a polymer/gel-like film as the result of a catalytically enhanced electrolyte reduction proposed by Tarascon [44], and formation of a lithium-gold alloy [45]. These factors give an extra reversible capacity to the reaction mechanism expressed in Equations (1) and (2) and may contribute to capacities exceeding the theoretical capacity. As for the first anodic process, peaks from about 1.1 to 2.2 V are associated with the reversible oxidation of Co to a series of cobalt oxides. The small peaks below 0.5 V are probably due to reactions with electrolyte at the electrode interface, and dealloying of the gold substrate. To evaluate these peaks, CV of the bare gold substrate and the Ni inverse opal coated gold electrodes were also conducted, as shown in Fig. 4c,d. Similar peaks below 0.5 V were observed, which can be ascribed to dealloying of gold [45]. No signal from NiO (usually ~0.5 V and ~1.2 V cathodic peaks which correspond to the initial reduction of NiO to metallic Ni, and the reduction of NiO in the following cycles, respectively [46]) or an ~2.3 V anodic peak [47]) in the CV of the Ni inverse opal on gold electrode was detected, indicating minimal oxidation of the Ni scaffold. From the second scan on, the cathodic peak shifts to 0.75 and 1.34 V are caused by reduction

of polarization after the first cycle. The similarity between the second and third cycle suggests that reactions 1 and 2 are reversible.

The galvanostatic charge and discharge performance of the Ni@Co₃O₄ nanosheet inverse opal electrode at a current density of 500 mA g⁻¹ for 50 cycles is shown in Fig. 6. The initial discharge and charge capacities are 1478 and 1224 mAh g⁻¹, respectively. The fact that the discharge capacity is much greater than the theoretical capacity value of Co₃O₄ (890 mAh g⁻¹) is probably due to the formation of an irreversible SEI layer, a reversible gel-like film on the surface of Co₃O₄ nanosheets, and the contribution from the lithium alloying reactions with gold (we will discuss the contribution from gold in greater detail in the following paragraph). We also speculate that the porous structure of the ultrathin Co₃O₄ nanosheets may provide additional sites for entrapment of lithium during the discharge process. Because of the high surface area of the Co₃O₄, lithium may be deposited on the surface of the Co₃O₄ in addition to inside the active material, as has been observed for other, usually carbonaceous materials [48], which would also increase the capacity [49, 50].

In Fig. 6a, the plateaus at about 1.2 and 0.8 V during the discharge process can be ascribed to the conversion from Co₃O₄ to an intermediate phase CoO and then to metallic Co, respectively. The plateau close to 0.1 V may be attributed to the reversible formation-dissolution of polymeric species on the surface of Co₃O₄ at low potential and the alloying reactions between lithium and gold, as previously discussed. The gold capacity contribution to the total capacity in Fig. 6a, was estimated taking into account the

electrochemical reaction potential ranges (shown in CV), the current density, and the gold mass (~ 0.23 mg, at a size of 2 cm^2 , 60 nm thick). The gold capacity also decays during cycling, which is consistent with the previous report [51]. From Fig. 6b, it is found that the first irreversible capacity loss (discharge) of the electrode is 18.7%. The first Coulombic efficiency is 87.5%, and it increases gradually to greater than 97% after 9 cycles. After that, the Coulombic efficiency remains around 98%. Even after 50 cycles at a current density of 500 mA g^{-1} (corresponding to 0.56C), the electrode still maintains a capacity of about 726 mAh g^{-1} (the measured capacity is 770 mAh g^{-1} , and the estimated capacity due to gold is about 44 mAh g^{-1} , see discussion in the SI following Fig. S3 for a more extensive discussion), which is much greater than the theoretical capacity of commercial graphite (372 mAh g^{-1}). Compared with a number of previous reports on anode nanomaterials (Table S1), the ultrathin Co_3O_4 nanosheet-grown 3D electrode appears to provide a competitive capacity and fast charge-discharge rates. The excellent cycling performance under high current densities is particularly interesting, as many emerging high energy density systems have significant capacity losses at high rates.

Fig. 6c shows the discharge capacities of the $\text{Ni@Co}_3\text{O}_4$ nanosheet inverse opal electrode at a series of charge-discharge current densities of about 571, 714, 1071, 1429, and 1786 mA g^{-1} . Even at 1786 mA g^{-1} the electrode has a capacity of 487 mAh g^{-1} (as previously noted, the capacity at 500 mA g^{-1} after 50 cycles was 726 mAh g^{-1}). When the current density is returned to 571 mA g^{-1} , the capacity recovers to 698 mAh g^{-1} . While 1786 mA g^{-1} does not correspond to a high C-rate compared to previous report [52], the capacity retention at a lower C-rate after high C-rate cycling indicates the high C-rate cycling does not damage the

electrode. Electrochemical impedance spectroscopy (EIS) was used to evaluate the electrical properties of the electrode (Fig. 6d). All impedances were measured at 3 V from 0.01 Hz to 100 kHz. The Nyquist plots consist of a semicircle in high frequency region which can be ascribed to the charge transfer process at the interfaces between electrolyte and electrode [53], and a straight line in the low frequency region. Prior to the first cycle, the electrode shows a smaller diameter semicircle relative to after 15 cycles, indicating that the charge transfer resistance increases with cycling, perhaps due to SEI formation. By fitting with an equivalent circuit model similar to previous literature reports [54, 55], the combination of surface film and charge transfer resistances (R_{sf+ct}) is determined to increase with cycling from 78 to 114 Ω . The capacitances before and after cycling are about 31 and 54 μF , respectively, which are close to some other anodes such as the carbon-coated ZnFe_2O_4 nanoparticles [56] and the Fe_2O_3 nanoflakes [57]. In the low frequency region, the slopes remain around 60° before and after cycling, indicating the Warburg impedance remains constant, suggesting stable contacts between active materials and the current collector and that the solid phase Li-ion diffusion processes remain constant [58]. The robust nature of the electrode after 50 cycles is also confirmed by electron microscopy. In the SEM images (Fig. S4), the structure of electrode appears to be retained even after numerous lithiation and delithiation cycles. The TEM observations (Fig. 7) indicate the nanosheets retain their layered and porous structure after 50 cycles. A thin SEI layer can be observed at the very edge (most clear in Fig. 7b), which is in agreement with other reports on cycled nanomaterial-based electrodes [59, 60]. We found the nanosheets remain tightly attached to the Ni scaffold after cycling (Fig. S5). Based on the morphological and electrical characterization, the rate and cycling performance of the

Ni@Co₃O₄ nanosheet inverse opal electrode can be attributed to the following: the ultrathin Co₃O₄ nanosheets provide short pathways for lithium and electrons, the electrode is mechanically stable, and the Ni scaffold provides good long-range electrical conductivity. In addition, the Co₃O₄ is attached to the surface of the porous 3D scaffold, minimizing its aggregation into larger particles. Based on the capacity measurements, it appears most of the electrochemically active material participates in the reactions with lithium.

In addition to the attributes listed above, for a number of applications, the voltage hysteresis is also important [61, 62] (perhaps less important for small portable devices, where the round-trip efficiency is less critical than total energy, and more important for large-scale applications, where good round-trip efficiency provides a significant financial benefit). A voltage hysteresis both leads to energy loss during cycling, and is an issue for battery management systems [63, 64]. While the full mechanism for hysteresis is not known, models, including one proposed by Gallagher et al. relate hysteresis and voltage fade to partially reversible migration of transition-metals and/or Li, driven by the presence of vacancies [65]. This model was subsequently supported by direct evidence of path-dependent lithium site occupation, correlated to structural reorganization of the metal oxide and electrochemical hysteresis during lithiation-delithiation [66]. Reddy et al. reported that a lower hysteresis was observed at higher temperature, which could be due to improved ionic conductivity of electrolyte and diffusivity of Li, as well as enhanced surface/interfacial reaction kinetics [45]. Other groups have also found that diffusion of multiple species is important [67]. From the CV data, we estimate the hysteresis of our electrode to be ~0.72 V, which is similar and perhaps better than other Co₃O₄-based anodes. For example, ~35 nm Co₃O₄ nanoparticles

showed a hysteresis of $\sim 0.83 \pm 0.03$ V at 0.2C) [68]. Our system provides efficient electron transport pathways, and good access of the active material to the electrolyte, however, clearly additional work is needed.

To evaluate the effect of Co_3O_4 loading and scaffold morphology, the electrochemical properties of an electrode grown with relatively thick (~ 20 nm thick) Co_3O_4 nanosheets and a Co_3O_4 film grown on Ni film were also prepared, as shown in Fig. S6. We note that the thickness of Co_3O_4 nanosheets can be easily controlled by adjusting the hydrothermal growth conditions, *e.g.* the concentration of reagents. All the three electrodes were cycled from 0.005 to 3 V at a current density of 500 mA g^{-1} . As shown in Fig. 8, the Ni@ Co_3O_4 nanosheet inverse opal electrode exhibits the best cycling performance of the three electrodes. The thick nanosheet inverse opal decays more significantly than the ultrathin nanosheet system; and the flat film structure fades even faster. The fact that a thicker layer of Co_3O_4 nanosheets reduces the electrode performance leads us to speculate that a higher surface area Ni inverse opal should be considered which would increase the mass loading of Co_3O_4 without increasing the thickness of the active layer.

4. Conclusions

A unique anode design based on of ultrathin Co_3O_4 nanosheets coated on a Ni inverse opal electrode was fabricated and characterized. The Co_3O_4 nanosheets grow uniformly throughout the 3D porous Ni inverse opal. The 4 nm thick nature of the nanosheets, about 4 nm, in addition to their mesoporous structure appears to be important for good performance. The Ni@ Co_3O_4 nanosheet inverse opal electrode provides a capacity of 726 mAh g^{-1} at a current

density of 500 mA g^{-1} even after 50 cycles. In addition, the capacity is 487 mAh g^{-1} when the charge-discharge current density is increased to 1786 mA g^{-1} . The performance under higher current densities can be attributed to the electrode architecture, which provides a short pathway for lithium and electrons in the Co_3O_4 , is mechanically stable, and gives good long-range electrical conductivity. Co_3O_4 aggregation can be effectively avoided because the Co_3O_4 is attached to the surface of the porous 3D scaffold, which enabling most of the active nanomaterials to take part in the electrochemical reactions. These attributes make the proposed anode electrode an interesting candidate design for secondary batteries.

Acknowledgments

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award # DE-FG02-07ER46471. Xingjiu Huang and Jinhui Liu acknowledge support of the State Key Project of Fundamental Research for Nanoscience and Nanotechnology of China (2011CB933700), and the One Hundred Person Project of the Chinese Academy of Sciences.

References

- [1] M. Thackeray, Nat. Mater. 1 (2002) 81-82.
- [2] B. Dunn, H. Kamath, J.M. Tarascon, Science 334 (2011) 928-935.

- [3] M.R. Palacin, Chem. Soc. Rev. 38 (2009) 2565-2575.
- [4] H. Yang, S. Amiruddin, H.J. Bang, Y.K. Sun, J.J. Prakash, Ind. Eng. Chem. 12 (2006) 12-38.
- [5] J.B. Goodenough, Acc. Chem. Res. 46 (2013) 1053-1061.
- [6] A. Mukhopadhyay, A. Tokranov, K.Sena, X.C. Xiao, B.W. Sheldon, Carbon 49 (2011) 2742-2749.
- [7] K.T. Lee, S. Jeong, J. Cho, Acc. Chem. Res. 46 (2013) 1161-1170.
- [8] N.N. Wang, X.J. Ma, H.Y. Xu, L. Chen, J. Yue, F.E Niu, J. Yang, Y.T. Qian, Nano Energ. 6 (2014) 193-199.
- [9] F.C. Zheng, Y. Yang, Q.W. Chen, Nat. Commun. 5 (2014) 5261.
- [10] B. Philippe, R. Dedryvere, M. Gorgoi, H. Rensmo, D. Gonbeau, K. Edstrom, J. Am. Chem. Soc. 135 (2013) 9829-9842.
- [11] H.B. Yao, G.Y. Zheng, W.Y. Li, M.T. McDowell, Z.W. Seh, N.A. Liu, Z.D. Lu, Y. Cui, Nano Lett. 13 (2013) 3385-3390.
- [12] S.H. Liu, H.P. Jia, L. Han, J.L. Wang, P.F. Gao, D.D. Xu, J. Yang, S.N. Che, Adv. Mater. 24 (2012) 3201-3204.
- [13] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, Nature 407 (2000) 496-499.
- [14] Y.L. Gong, M. Zhang, G.Z. Cao, RSC Adv. 5 (2015) 26521-26529.
- [15] M.V. Reddy, G.V.S. Rao, B.V.R. Chowdari, Chem. Rev. 113 (2013) 5364-5457.
- [16] C. Rosant, B. Avasle, D. Larcher, L. Dupont, A. Friboulet, J.M. Tarascon, Energ. Environ. Sci. 5 (2012) 9936-9943.

- [17] H.W. Shim, Y.H. Jin, S.D. Seo, S.H. Lee, D.W. Kim, *ACS Nano* 5 (2011) 443-449.
- [18] Z.Y. Wang, L. Zhou, X.W. Lou, *Adv. Mater.* 24 (2012) 1903-1911.
- [19] M.H. Chen, X.H. Xia, J.H. Yin, Q.G. Chen, *Electrochim. Acta* 160 (2015) 15-21.
- [20] M.V. Reddy, B.C. Zhang, L.J.E. Nichollette, K.M. Zhang, B.V.R. Chowdari, *Electrochem. Solid State Lett.* 14 (2011) A79-A82.
- [21] H.W. Che, A.F. Liu, *J. Mater. Sci. Mater. Electron.* 26 (2015) 4097-4104.
- [22] K.Q. Zhou, J.J. Liu, P.Y. Wen, Y. Hu, Z. Gui, *Mater. Res. Bull.* 67 (2015) 87-93.
- [23] F.X. Wang, L. Liang, L. Shi, M.S. Liu, J.M. Sun, *J. Alloy Compd.* 633 (2015) 65-70.
- [24] M.V. Reddy, B.C. Zhang, K.P. Loh, B.V.R. Chowdari, *CrystEngComm* 15 (2013) 3568-3574.
- [25] M.V. Reddy, G. Prithvi, P.L. Kian, B.V.R. Chowdari, *ACS Appl. Mater. Interfaces* 6 (2014) 680-690.
- [26] X. Li, G.L. Xu, F. Fu, Z. Lin, Q. Wang, L. Huang, J.T. Li, S.G. Sun, *Electrochim. Acta* 96 (2013) 134-140.
- [27] R.B. Rakhi, W. Chen, D. Cha, H.N. Alshareef, *Nano Lett.* 12 (2012) 2559-2567.
- [28] Y. Liu, C.H. Mi, L.H. Su, X.G. Zhang, *Electrochim. Acta* 53 (2008) 2507-2513.
- [29] J. Liu, H. Xia, L. Lu, D.F. Xue, *J. Mater. Chem.* 20 (2010) 1506-1510.
- [30] Y. Wang, Y.J. Bai, X. Li, Y.Y. Feng, H.J. Zhang, *Chem. Eur. J.* 19 (2013) 3340-3347.
- [31] A.K. Rai, J. Gim, L.T. Anh, J. Kim, *Electrochim. Acta* 100 (2013) 63-71.
- [32] C.T. Hsieh, J.S. Lin, Y.F. Chen, H.S. Teng, *J. Phys. Chem. C* 116 (2012) 15251–15258.
- [33] H.G. Zhang, P.V. Braun, *Nano Lett.* 12 (2012) 2778-2783.
- [34] J.H. Pikul, H.G. Zhang, J. Cho, P.V. Braun, W.P. King, *Nat. Commun.* 4 (2013) 1732.

- [35] X.D. Yu, Y.J. Lee, R. Furstenberg, J.O. White, P.V. Braun, *Adv. Mater.* 19 (2007) 1689-1692.
- [36] H.G. Zhang, X.D. Yu, P.V. Braun, *Nat. Nanotechnol.* 6 (2011) 277-281.
- [37] L.M. Wang, B. Liu, S.H. Ran, H.T. Huang, X.F. Wang, B. Liang, D. Chen, G.Z. Shen, *J. Mater. Chem.* 22 (2012) 23541-23546.
- [38] Y. Yu, L.H. Chen, B.L. Su, *J. Mater. Chem. A* 2 (2014) 9699-9708.
- [39] X. Huang, J. Chen, Z.Y. Lu, H. Yu, Q.Y. Yan, H.H. Hng, *Sci. Rep.* 3 (2013) 2317.
- [40] H. Nishihara, T. Kyotani, *Adv. Mater.* 24 (2012) 4473-4498.
- [41] Y. Liu, X.G. Zhang, *Electrochim. Acta* 54 (2009) 4180-4185.
- [42] D. Larcher, G. Sudant, J.B. Leriche, Y. Chabre, J.M. Tarascon, *J. Electrochem. Soc.* 149 (2002) A234-A241.
- [43] V. Pralong, J.B. Leriche, B. Beaudoin, E. Naudin, M. Morcrette, J.M. Tarascon, *Solid State Ionics* 166 (2004) 295-305.
- [44] S. Laruelle, S. Grugeon, P. Poizot, M. Dolle, L. Dupont, J.M. Tarascon, *J. Electrochem. Soc.* 149 (2002) A627-A634.
- [45] M.V. Reddy, B. Pecquenard, P. Vinatier, A. Levasseur, *Electrochem. Commun.* 9 (2007) 409-415.
- [46] B. Varghese, M.V. Reddy, Y.W. Zhu, C. S. Lit, T. C. Hoong, G.V.S. Rao, B.V.R. Chowdari, A.T.S. Wee, C.T. Lim, C.H. Sow, *Chem. Mater.* 20 (2008) 3360-3367.
- [47] X.H. Wang, L. Qiao, X.L. Sun, X.W. Li, D.K. Hu, Q. Zhang, D.Y. He, *J. Mater. Chem. A* 1 (2013) 4173-4176.
- [48] K. Tokumitsu, H. Fujimoto, A. Mabuchi, T. Kasuh, *Carbon* 37 (1999) 1599-1605.

- [49] S. Nam, S. Kim, S. Wi, H. Choi, S. Byun, S.M. Choi, S.I. Yoo, K.T. Lee, B. Park, J. Power Sources 211 (2012) 154-160.
- [50] L.F. Shen, H.S. Li, E. Uchaker, X.G. Zhang, G.Z. Cao, Nano Lett. 12 (2012) 5673-5678.
- [51] L. Yuan, H.K. Liu, A. Maarroof, K. Konstantinov, J. Liu, M. Cortie, J. New Mat. Electrochem. Systems 10 (2007) 95-99.
- [52] X.H. Rui, H.T. Tan, D.H. Sim, W.L. Liu, C. Xu, H.H. Hng, R. Yazami, T.M. Lim, Q.Y. Yan, J. Power Sources 222 (2013) 97-102.
- [53] D.W. Su, J. Horvat, P. Munroe, H. Ahn, A.R. Ranjbartoreh, G.X. Wang, Chem. Eur. J. 18 (2012) 488-497.
- [54] M.V. Reddy, G.V.S. Rao, B.V.R. Chowdari, J. Mater. Chem. 21 (2011) 10003-10011.
- [55] B. Das, M.V. Reddy, C. Krishnamoorthi, S. Tripathy, R. Mahendiran, G.V.S. Rao, B.V.R. Chowdari, Electrochimica Acta 54 (2009) 3360-3373.
- [56] F. Martinez-Julian, A. Guerrero, M. Haro, J. Bisquert, D. Bresser, E. Paillard, S. Passerini, G. Garcia-Belmonte, J. Phys. Chem. C 118 (2014) 6069-6076.
- [57] M.V. Reddy, T. Yu, C.H. Sow, Z.X. Shen, C.T. Lim, G.V.S. Rao, B.V.R. Chowdari, Adv. Funct. Mater. 17 (2007) 2792-2799.
- [58] H.C. Tao, M. Huang, L.Z. Fan, X. H. Qu, Electrochim. Acta 89 (2013) 394-399.
- [59] D. Barreca, G. Carraro, A. Gasparotto, C. Maccato, M. Cruz-Yusta, J.L. Gomez-Camer, J. Morales, C. Sada, L. Sanchez, ACS Appl. Mater. Interfaces 4 (2012) 3610-3619.
- [60] C.T. Cherian, M.V. Reddy, S.C. Haur, B.V.R. Chowdari, ACS Appl. Mater. Interfaces 5 (2013) 918-923.
- [61] P.L. Taberna, S. Mitra, P. Poizot, P. Simon, J.M. Tarascon, Nat. Mater. 5 (2006) 567-573.

- [62] M. Sathiya, A.M. Abakumov, D. Foix, G. Rousse, K. Ramesha, M. Saubanere, M.L. Doublet, H. Vezin, C.P. Laisa, A.S. Prakash, D. Gonbeau, G. VanTendeloo, J.M. Tarascon, Nat. Mater. 14 (2015) 230-238.
- [63] D. Peralta, J.F. Colin, A. Boulineau, L. Simonin, F. Fabre, J. Bouvet, P. Feydi, M. Chakir, M. Chapuis, S. Patoux, J. Power Sources 280 (2015) 687-694.
- [64] J. Cabana, L. Monconduit, D. Larcher, M.R. Palacin, Adv. Energy Mater. 22 (2010) E170-192.
- [65] K.G. Gallagher, J.R. Croy, M. Balasubramanian, M. Bettge, D.P. Abraham, A.K. Burrell, M.M. Thackeray, Electrochem. Commun. 33 (2013) 96-98.
- [66] F. Dogan, B.R. Long, J.R. Croy, K.G. Gallagher, H. Iddir, J.T. Russell, M. Balasubramanian, B. Key, J. Am. Chem. Soc. 137 (2015) 2328-2335.
- [67] U. Boesenberg, M.A. Marcus, A.K. Shukla, T.H. Yi, E. McDermott, P.F. Teh, M. Srinivasan, A. Moewes, J. Cabana, Sci. Rep. 4 (2014) 7133.
- [68] A. Ponrouch, M.R. Palacin, J. Power Sources 212 (2012) 233-246.

Figure captions:

Scheme 1. Illustration of the Ni@Co₃O₄ nanosheet inverse opal anode fabrication procedure.

Fig. 1. SEM images of (a) polystyrene opal after heating at 95 °C for 3 h, and (b) Ni inverse opal after removing the polystyrene opal template. (c) Low- and (d) high-magnification top-view SEM images of the Ni@Co₃O₄ inverse opal; (e) low- and (f) high-magnification cross-sectional SEM images of the Ni@Co₃O₄ inverse opal.

Fig. 2. Glancing angle XRD collected from a Ni@Co₃O₄ inverse opal. The inset was recorded through a normal XRD scan mode.

Fig. 3. (a), (b) TEM and (c) HRTEM images of Co₃O₄ nanosheets from a Ni@Co₃O₄ inverse opal electrode. The cross-sectional thickness and lattice fringe spacings are indicated in (c). (d) SAED from a region which included (c).

Fig. 4. Elemental distributions in the Ni@Co₃O₄ nanosheet inverse opal electrode: (a) Cross-section SEM image; (b) elemental distribution of Co K α corresponding to (a); (c) Elemental distribution of Ni K α corresponding to (a).

Fig. 5. First three CV cycles of (a) the Ni@Co₃O₄ nanosheet inverse opal, (b) the bare gold substrate (no Ni and Co₃O₄) and (c) the Ni inverse opal on gold (without Co₃O₄ coating) electrodes over the potential range of 0.0 to 3.0 V vs. Li⁺/Li at a scan rate of 0.1 mV s⁻¹.

Fig. 6. Cycling performance of the Ni@Co₃O₄ nanosheet inverse opal electrode: (a) the galvanostatic charge-discharge curves at a current density of 500 mA g⁻¹; (b) corresponding charge and discharge capacities and Coulombic efficiency; (c) rate capacities at different current densities. All values in (b) and (c) have been calibrated by removal of the estimated gold capacities. (d) Nyquist plots of the electrode before and after 15 charge-discharge cycles. The current density of the charge-discharge cycling was 500 mA g⁻¹. The fitted equivalent circuits with all the elements are shown in the inset (R_e : electrolyte resistance; R_{sf+ct} : surface film+charge transfer resistance; CPE_{sf+ct} : constant phase element; W : Warburg resistance; C_{int} : intercalation capacitance).

Fig. 7. (a) TEM image of a Co₃O₄ nanosheet removed from a Ni@Co₃O₄ inverse opal electrode after 50 cycles at a current density of 500 mA g⁻¹. (b) Higher magnification TEM image at the edge of a nanosheet. (c) Higher magnification TEM image from the center region of a nanosheet.

Fig. 8. Comparison of the capacity performance during charge and discharge cycling from 0.005 to 3 V at a current density of 500 mA g⁻¹ for the Ni@Co₃O₄ nanosheet inverse opal, the Ni@thick Co₃O₄ nanosheet inverse opal, and a Co₃O₄-coated Ni film. Scale bars in insets are 100 nm. Values include removal of the estimated capacity due to the gold.

Abstract graphic:

Scheme 1.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8