CoO-Co nanocomposite anode with enhanced electrochemical performance for lithium-ion batteries

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Abstract

CoO-Co nanocomposite films were successfully deposited at room temperature by pulsed laser deposition as an anode material for lithium-ion batteries. The prepared nanocomposite exhibited enhanced performance, such as excellent cycling stability (830 mA h g^{-1} at a specific current of 500 mA g^{-1} after 200 cycles) and high rate capability (578 mA h g^{-1} at 10000 mA g^{-1}). The outstanding electrochemical performance can be ascribed to the nanocrystalline structure of CoO and the presence of Co nanoparticles, which could sustain high strain, enhance reaction kinetics and improve conductivity.

1. Introduction

Driven by ever-increasing applications of lithium-ion batteries (LIBs) in portable electronics and electric vehicles, there has been intense interest in developing advanced electrode materials with higher energy and power densities in recent years [1-3]. To date, various materials (such as graphitic carbons, Si, Sn, and metal oxides) have been exploited as anodes based on different electrochemical mechanisms including intercalation, alloying, and conversion reactions [4-13]. Among them, 3d transition metal oxides (TMOs, i.e. CoO, Fe₂O₃, NiO, and CuO) have been widely investigated as anode materials for lithium-ion batteries because of their larger theoretical capacity and better safety in comparison with conventional carbon-based materials [11-17]. However, the significant volume change and the poor electronic conductivity of transition metal oxides (TMOs) lead to capacity fade and poor performance at high rates, which limits their applications in storage energy system [18-20]. Meanwhile, an usually large hysteresis between the discharge and charge steps leads to a high degree of round-tip energy inefficiency [21, 22] and the absence of stable solid electrolyte interface (SEI) film results in a rapid capacity fading due to continuous electrolyte decomposition [23, 24].

To circumvent these problems, many strategies have been developed. One potential strategy is to design TMOs with various morphologies on the nanoscale to shorten the lithium-ion diffusion distance and buffer the mechanical strain during cycles [25-31]. TMOs with various structures (such as nanowires, nanobelts, nanosheets, hollow spheres and nanocrystalline films) have shown considerable

improvements in the reversible capacity. Another effective strategy is combining TMOs with conductive carbon or metal materials, thus improving the conductivity and relaxing the volume expansion/contraction of metal oxides during cycling [32-36]. It has been widely reported that nanosize transition metals can facilitate the electrochemical kinetics of lithium conversion reactions [23, 37-39]. Wang *et al.* demonstrated that the nanosize transition metal in lithium conversion compounds can provide a highly conductive pathway for local electron transport necessary for conversion reaction [40, 41]. Based on the previous reports, nanocrystalline TMOs embedded with nanosize transition metal are expected to possess improved performance in cycling stability and rate capability, resulting from the combination of nanostructure engineering and hybridization strategies. In NiO-Ni nanocomposite, Li *et al.* observed good cyclability and rate capability [37]. Bresser *et al.* fabricated CoO-Co-C nanocomposite with enhanced long-term cycling stability and coulombic efficiency [23]. Zhang *et al.* also achieved excellent cycle stability and high rate capacity in Co-CoO_x nanowire arrays [42]. However, the control over particle size and distribution in the nanoassembly is still challenging due to the complicated synthetic procedure, which may involve synthesis of specific templates, impregnation of precursors and template removal.

In this paper, we propose to assemble nanosize transition metal into nanocrystalline TMO film anodes using pulsed laser deposition (PLD). As a typical TMO anode, CoO has been widely investigated since its discovery [11], and is selected as a prototype anode in our work. The nanocrystalline structure of CoO

1 anode does not only enhance reversibility of conversion reaction but also relax
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3 volume expansion/contraction during cycling. In the meantime, the uniformly
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5 distributed Co nanoparticles can improve the electronic conductivity and facilitate a
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7 more complete decomposition of the Li_2O . Therefore, the prepared CoO-Co
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9 nanocomposites show high reversible capacity of 830 mA h g^{-1} at 500 mA g^{-1} and
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11 good rate capability of 578 mA h g^{-1} at 10000 mA g^{-1} . The remarkable
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13 electrochemical performance and facile synthesis demonstrate that the CoO-Co
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15 composite has potential applications in high performance LIBs, especially in
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17 all-solid-state thin film batteries.
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25 **2. Experiments**

26 **2.1. Synthesis of nanocomposite CoO films with embedded Co nanoparticles**

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28 The nanocomposite CoO-Co films were deposited on copper foil by a PLD
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30 technique under a base pressure of $1.0 \times 10^{-5} \text{ Pa}$. A KrF excimer laser with wavelength
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32 of 248 nm was used to ablate the cobalt metal target (99.99 %, KeJing Group)
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34 operating with a pulse repetition rate of 6 Hz and energy of 400 mJ/pulse. To obtain
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36 nanocrystalline CoO films, we grown samples at room temperature under oxygen
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38 pressure of 0.2 Pa and 0.3 Pa respectively. At oxygen pressure of 0.2 Pa, films were
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40 only partially oxidized with embedded metal Co. The thickness of the nanocomposite
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42 film is approximately 200 nm as determined by atomic force microscope (AFM, Park
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44 systems XE7). The mass of 0.152 mg was obtained by measuring the difference of
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46 substrate before and after deposition via electrobalance (METTLER TOLEDO).
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59 **2.2. Material characterization**

The crystal structure of the resulted films were determined by a Rigaku D/Max X-ray diffractometer with filtered Cu K α radiation at a voltage of 40 kV and a current of 40 mA. High-resolution transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were collected on a FEI Tecnai G2 F20 instrument. The surface morphology was characterized by field emission scanning electron microscope (SEM) using a JSM-6700F. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250XI photoelectron spectrometer. Magnetization measurements were performed by a Physical Property Measurement System (PPMS).

2.3. Electrochemical measurements

Electrochemical performance of CoO-Co nanocomposites was evaluated using CR-2032-type coin cells (KeJing Group), which were assembled inside an argon-filled glove box with a lithium foil (KeJing Group) as counter and a Celgard 2250 film as separator. The electrolyte solution was a standard electrolyte of 1: 1: 1 ethylene carbonate (EC)/propylene carbonate (PC)/dimethyl carbonate (DMC)/ LiPF₆ (KeJing Group). Charge-discharge characteristics were conducted by a LAND-ct2001A battery system at various current rates between 0.01 V and 3.0 V at room temperature. Cyclic voltammetry (CV) measurements were performed in a potential range of 0.01 V-3.0 V at sweep rates of 0.1 mV s⁻¹ using a CHI660E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) data was obtained on the same electrochemical workstation by applying a 5 mV amplitude signal from 100 kHz to 0.01 Hz.

3. Results and discussion

The XRD pattern of CoO-Co nanocomposite is shown in Fig. 1a. Except for the diffraction reflections corresponding to copper foils, no obvious diffraction reflections of crystalline CoO can be observed. This indicates that the composite is amorphous or crystallized with small grain size. In order to investigate the chemical composition, XPS measurement has been performed. Fig. 1b shows the Co2p XPS spectrum of CoO-Co composition. The peaks of Co 2p_{3/2} located at 780.5 eV and Co 2p_{1/2} locate at 796.6 eV indicate the formation of CoO [43, 44]. The oxidation state of CoO are further confirmed by the appearance of strong peaks of shake-up satellites. However, there are no peaks for Co⁰, which can be attributed to the following two reasons. Firstly, the peaks for Co⁰ located at 778.4 eV are quite close to the Co²⁺ peaks located at 780.5 eV. Secondly, the quantity of metallic cobalt in the sample is much lower than the oxide cobalt quantity. Although no peaks for Co⁰ are observed due to limitation of XPS sensitivity, magnetism measurement of this composite in Fig. 1c shows room temperature ferromagnetism with a saturation magnetization of 22 emu/cm³. On the contrary, films grown at higher oxygen pressure of 0.3 Pa were almost totally oxidized into CoO and displayed negligible ferromagnetism as shown in Fig. 1c. These results reveal that the existence of Co pure metal in the CoO films grown under oxygen pressure of 0.2 Pa since no ferromagnetism could be observed in oxides of cobalt at room temperature [45, 46]. To further confirm its microstructure, TEM characterization was conducted as shown in Fig. 2. The polycrystalline nature of CoO-Co nanocomposite is confirmed by the ring-like feature of the selected area

electron diffraction (SAED), which can be assigned to CoO and Co. The CoO and Co nanograins are around 5-10 nm in sizes as confirmed by the HRTEM. Based on the above results, it can be concluded that the film is composed of the nanocrystalline CoO and Co particles and the Co metal particles are dispersed in the CoO matrix.

The electrochemical property of electrodes made of CoO-Co composition was examined by cyclic voltammetry (CV). The CV curves are similar to the previous reports of CoO anode [42, 47]. Fig. 3 shows the first five CV curves at a scan rate of 0.1 mV s⁻¹. In the first cathodic scan, a strong peak at 1.0 V relates to the reduction of CoO into Co and the formation of SEI film. Meanwhile, an oxidation peak appears at 2.0 V in the anodic process, which results from the decomposition of Li₂O by Co. In the subsequent cycles, the basically overlapped CV curves represent the excellent electrochemical reversibility of CoO-Co electrode. The reduction of CoO to Co is realized at higher voltages around 1.1 V due to the amorphization of CoO followed by the formation of ultrafine nanograins during the first cycle [11]. It is worth noting that the weak peaks at about 0.95 V may result from the SEI formation. Correspondingly, a weak anodic peak relating to the reversible decomposition of SEI locates at about 1.5 V. This could be attributed to the significant chemical catalysis of origin Co particles for the reversible conversion of some SEI components, which has been reported previously in Co@CoO core-shell and Ni/SnO₂ nanocluster [42, 48].

Fig. 4a shows the charge/discharge cycling performance of CoO-Co. The cycling stability was evaluated up to 200 cycles between 0.01 V and 3.0 V at a specific current of 500 mA g⁻¹ at room temperature. As shown in Fig. 4b, obvious voltage

hysteresis are observed due to the conversion reaction during charge/discharge processes and the voltage plateaus are in good agreement with the above CV results. In the first discharge, the long plateau at about 1.0 V is attributed to the reduction of CoO to Co. An initial discharge capacity of 963 mA h g⁻¹ and a reversible charge capacity of 656 mA h g⁻¹ are delivered, indicating a Coulombic efficiency of 68.1 %. The irreversible capacity loss is mainly attributed to the formation of SEI layer on the surface of anode. Nevertheless, the Coulombic efficiencies are about 99.6 % during the following cycles as shown in Fig. 4b. This good cycling stability demonstrates an excellent structural stability of nanocrystalline CoO with size of several nanometers. The nanoscale electrode structure can improve the capacity to sustain high lithium insertion strain because of the smaller number of atoms and large surface areas within nanoparticles [9, 14]. As shown in Fig. 5, the CoO-Co film keeps good structure integrity except for some minor cracks after many cycles. Meanwhile, the cobalt metal also played an important role on improving the cycle stability. As shown in Fig. 6, the pure CoO anode without cobalt metal grown under 0.3 Pa suffers from faster capacity fading, degrading from 732 mAh g⁻¹ at the second cycle to only 635 mAh g⁻¹ at the 125th cycle.

Furthermore, it is mentionable that the discharge capacities gradually increased to 871 mA h g⁻¹ during the first 140 cycles and then slightly decreased to 830 mA h g⁻¹ after 200 cycles, which is much higher than the theoretical value of CoO (716 mA h g⁻¹). The discharge curves below 1.0 V decay slower and slower during the first 140 cycles as shown in Fig. 4b, contributing the extra electrochemical capacity. Similar

capacity rise phenomena during cycling has been observed from transition-metal oxide composite anode materials [10, 14, 49-54]. The increasement of capacity can be ascribed to the formation of polymeric gel-like films through the electrolyte decomposition [51], the storage of Li-containing SEI layer [55], defect-induced storage of lithium-ions [56], and interfacial lithium storage between metallic nanoparticles and Li_2O [57]. Among them, the reversible growth of polymer/gel-like films has been widely accepted as the dominant factor to increase the capacity at low potentials [51, 58]. Such polymeric films result from kinetically active electrolyte degradation during conversion process and its activity depends on the catalytic activity of metallic nanograins [51, 59]. However, it would also result in a rapid capacity fading when decreasing the amount of electrolyte, because the cell would simply run dry.

The CoO-Co composite electrodes also exhibited excellent rate performance. Fig. 6a shows the rate capabilities at various specific currents from 500 mA g^{-1} to 10000 mA g^{-1} in a voltage window of 0.01 V-3.0 V. The anode delivered capacities up to 706 mA h g^{-1} , 673 mA h g^{-1} and 578 mA h g^{-1} at high current densities of 1000 mA g^{-1} , 5000 mA g^{-1} , and 10000 mA g^{-1} respectively, which is corresponding to 99.4 %, 94.7 %, and 80 % retention of the capacity at 500 mA g^{-1} (about 710 mA h g^{-1}). More importantly, when the specific current reduced to 500 mA g^{-1} , the capacity could recover to 753 mA h g^{-1} . These results indicate higher reversibility of the lithiation/delithiation reaction at high rates than those reported pure TMOs film anodes [60-62]. The excellent rate performance benefits from both nanocrystalline

CoO reducing diffusion length [63], and embedded Co nanoparticles promoting the decomposition of Li_2O [37, 40-42].

To confirm the role of cobalt nanoparticles in the superior rate capability, we also rate performance of CoO anode deposited under an oxygen pressure of 0.3 Pa. As shown in Fig. 7a, the capacities of CoO anode without Co dropped to 431 mA h g^{-1} upon increasing the specific current to 10000 mA g^{-1} , which was about 59.6 % of the value at 500 mA g^{-1} (736 mA h g^{-1}). Meanwhile, electrochemical impedance spectroscopy (EIS) measurement was performed to gain further insight into the electrochemical performance. Fig. 7b shows the comparison of impedance plots of CoO anodes grown at different oxygen pressure. Both impedance spectra consist of single semicircle in the high-middle frequency region and a sloping line in the low-frequency region, representing the charge-transfer impedance in the electrode/electrolyte and lithium-diffusion process of the electrodes [64, 65]. Obviously, the diameter of the semicircle for anode grown at 0.2 Pa is much smaller than that for anode grown at 0.3 Pa, indicating a lower contact and charge-transfer resistance in the high and medium frequency region. On the other hand, the larger slope at low frequencies of the CoO-Co electrode indicates high Li^+ ion mobility in the solid phase [66]. All these results confirm that the uniformly distributed Co nanoparticles play a critical role in the rate performance benefited from their good electrical conductivity and significant catalytic effect on the decomposition of Li_2O .

4. Conclusions

In summary, nanocrystalline CoO-Co film anodes have been deposited by pulsed

laser deposition for the first time. Characterization results show that the anode is composed of nanocrystalline CoO and Co particles with average size of 5-10 nm. The prepared composites anode exhibited good cycling stability (830 mA h g⁻¹ at a specific current of 500 mA g⁻¹ after 200 cycles) and superior rate capability (578 mA h g⁻¹ at 10000 mA g⁻¹). The outstanding electrochemical performance can be ascribed to the Co nanoparticles acting as highly conductive medium. Meanwhile, the nanograins of CoO with large exposed surface areas and small number of atoms enable a reversible electrochemical behavior. The remarkable electrochemical performance and room temperature growth demonstrate that the binder-free nanocrystalline CoO-Co has potential applications in high performance LIBs, especially in all-solid-state thin film batteries.

Acknowledgments

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References

- [1] M. Armand, J. M. Tarascon, Building better batteries, *Nature* 451 (2008) 652-657.
- [2] J. B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, *Chem. Mater.* 22 (2010) 587-603.

- [3] T. Y. Tang, Y. Y. Zhang, W. L. Li, B. Ma, X. D. Chen, Rational material design for ultrafast rechargeable lithium-ion batteries, *Chem. Soc. Rev.* 44, (2015) 5926-5940.
- [4] X. Huang, Z. Y. Zeng, Z. X. Fan, J. Q. Liu, H. Zhang, Graphene-based electrodes, *Adv. Mater.* 24 (2012) 5979-6004.
- [5] U. Kasavajjula, C. Wang, A. J. Appleby, Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells, *J. Power. Sources* 163 (2007) 1003-1039.
- [6] M. Winter, J. O. Besenhard, Electrochemical lithiation of tin and tin-based intermetallics and composites, *Electrochim. Acta*, 45 (1999) 31-50.
- [7] X. Zhou, L. J. Wan, Y. G. Guo, Binding SnO₂ nanocrystals in nitrogen-doped graphene sheets as anode materials for lithium-ion batteries, *Adv. Mater.* 25 (2013) 2152-2157.
- [8] J. Jiang, Y. Y. Li, J. P. Liu, X. T. Huang, C. Z. Yuan, X. W. Low, Recent advances in metal oxide-based electrode architecture design for electrochemical energy storage, *Adv. Mater.* 24 (2012) 5166-5180.
- [9] H. B. Wu, J. S. Chen, H. H. Hng, X. W. Lou, Nanostructured metal oxide-based materials as advanced anodes for lithium-ion batteries, *Nanoscale* 4 (2012) 2526-2542.
- [10] S. H. Yu, S. H. Lee, D. J. Lee, Y. E. Sung, T. Hyeon, Conversion reaction-based oxide nanomaterials for lithium ion battery anodes, *Small* 12 (2016) 2146-2172.

- [11] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature* 407 (2000) 496-499.
- [12] M. Winter, J. O. Besenhard, M. E. Spahr, P. Novak, Insertion electrode materials for rechargeable lithium batteries. *Adv. Mater.* 10 (1998) 725-763.
- [13] M. N. Obrovac, V. L. Chevrier, Alloy negative electrodes for Li-Ion batteries. *Chem. Rev.* 114 (2014) 11444-11502.
- [14] Y. Z. Jiang, D. Zhang, Y. Li, T. Z. Yuan, N. Bahlawane, C. Liang, W. P. Sun, Y. H. Lu, M. Yan, Amorphous Fe_2O_3 as a high-capacity, high-rate and long-life anode material for lithium ion batteries, *Nano Energy* 4 (2014) 23-30.
- [15] Z. Bai, Z. Ju, C. Guo, Y. Qian, B. Tang, S. Xiong, Direct large-scale synthesis of 3D hierarchical mesoporous NiO microspheres as high-performance anode materials for lithium ion batteries, *Nanoscale* 6 (2014) 3268-3273.
- [16] J. Y. Xiang, J. P. Tu, L. Zhang, Y. Zhou, X. L. Wang, S. J. Shi, Self-assembled synthesis of hierarchical nanostructured CuO with various morphologies and their application as anodes for lithium ion batteries, *J. Power. Sources* 195 (2010) 313-319.
- [17] T. V. Thi, A. K. Rai, J. Gim, J. Kim, High performance of Co-doped NiO nanoparticle anode material for rechargeable lithium ion batteries, *J. Power. Sources*, 292 (2015) 23-30.
- [18] Z. W. Lou, D. Deng, J. Y. Lee, J. Feng, L. Archer, Self-supported formation of needlelike Co_3O_4 nanotubes and their application as lithium-ion battery electrodes, *Adv. Mater.* 20 (2008) 258-262.

- [19] Z. Y. Wang, L. Zhou, X. W. Lou, Metal oxide hollow nanostructures for lithium-ion batteries, *Adv. Mater.* 24 (2012) 1903-1911.
- [20] J. Liang, H. Hu, H. Park, C. Xiao, S. Ding, U. Paik, X.W. Lou, Construction of hybrid bowl-like structures by anchoring NiO nanosheets on flat carbon hollow particles with enhanced lithium storage properties, *Energy Environ. Sci.* 8 (2015) 1707-1711.
- [21] J. Cabana, L. Monconduit, D. Larcher, M. R. Palacín, Beyond intercalation-based Li-Ion batteries: the state of the art and challenges of electrode materials reacting through conversion reactions, *Adv. Mater.* 22 (2010) E170..
- [22] L.S. Li, R. Jacobs, P. Gao, L. Y. Gan, F. Wang, D. Morgan, S. Jin, Origins of large voltage hysteresis in high-energy-density metal fluoride lithium-ion battery conversion electrodes. *J. Am. Chem. Soc.* 138 (2016), 2838-2848.
- [23] D. Bresser, E. Paillard, P. Niehoff, S. Krueger, F. Mueller, M. Winter, S. Passerini, Challenges of "going nano": Enhanced electrochemical performance of cobalt oxide nanoparticles by carbothermal reduction and in situ carbon coating. *Chemphyschem* 15 (2014), 2177-2185.
- [24] S. Grugeon, S. Laruelle, L. Dupont, J. M. Tarascon, An update on the reactivity of nanoparticles Co-based compounds towards Li, *Solid State Sci.* 5 (2003), 895. [25] Q. Lin, Y. J. Sha, B. T. Zhao, Y. B. Chen, M. O. Tade, Z. P. Shao, In situ electrochemical creation of cobalt oxide nanosheets with

- favorable performance as a high tap density anode material for lithium-ion batteries, *Electrochim. Acta* 180, (2015) 914-921.
- [26] L. Tian, H. L. Zou, J. X. Fu, X. F. Yang, Y. Wang, H. L. Guo, X. H. Fu, C. L. Liang, M. M. Wu, P. K. Shen, Q. M. Gao, Topotactic conversion route to mesoporous quasi-single-crystalline Co_3O_4 nanobelts with optimizable electrochemical performance, *Adv. Funct. Mater.* 20 (2010) 617-623.
- [27] H. Guan, X. Wang, H. Q. Li, C. Y. Zhi, T. Y. Zhai, Y. Bando, D. Golberg, CoO octahedral nanocages for high-performance lithium ion batteries, *Chem. Commun.* 48 (2012) 4878-4880.
- [28] H. Sun, G. Xin, T. Hu , M. Yu , D. Shao , X. Sun, J. Lian, High-rate lithiation-induced reactivation of mesoporous hollow spheres for long-lived lithium-ion batteries, *Nat. Commun.* 5 (2014) 4526.
- [29] B. Wang, H. B. Wu and L. Zhang, X. W. Lou, Self-supported construction of uniform Fe_3O_4 hollow microspheres from nanoplate building blocks, *Angew. Chem. Int. Ed.* 52 (2013) 4165-4168.
- [30] S. H. Lee, S.-H. Yu, J. E. Lee, A. Jin, D. J. Lee, N. Lee, H. Jo, K. Shin, T.-Y. Ahn, Y.-W. Kim, H. Choe, Y.-E. Sung, T. Hyeon, Self-assembled Fe_3O_4 nanoparticle clusters as high-performance anodes for lithium ion batteries via geometric confinement, *Nano Lett.* 13 (2013) 4249–4256.
- [31] Y. Wang, Q. Z. Qin, A nanocrystalline NiO thin-film electrode prepared by pulsed laser ablation for Li-ion batteries, *J. Electrochem. Soc.* 149 (2002) A873-A878.

- [32] L. Huang, R. Z. Wang, D. Xu, Z. L. Wang, H. G. Wang, J. J. Xu, Z. Wu, Q. C. Liu, Y. Zhang, X. B. Zhang, Homogeneous CoO on graphene for binder-free and ultralong-life lithium ion batteries, *Adv. Funct. Mater.* 23 (2013) 4345-4353.
- [33] Y. Qi, N. Du, H. Zhang, X. Fan, Y. Yang, D. R. Yang, CoO/NiSi(x) core-shell nanowire arrays as lithium-ion anodes with high rate capabilities, *Nanoscale*, 4 (2012) 991.
- [34] Y. Huang, Z. X. Lin, M. B. Zheng, T. H. Wang, J. Z. Yang, F. S. Yuan, X. Y. Lu, L. Liu, D. P. Sun, Amorphous Fe₂O₃ nanoshells coated on carbonized bacterial cellulose nanofibers as a flexible anode for high-performance lithium ion batteries, *J. Power. Sources* 307 (2016) 649-656.
- [35] X. N. Li, X. D. Ding, J. J. Hu, S. F. Wei, Z. H. Jiang, J. S. Lian, G. Y. Wang, Q. Jiang, J. A. Liu, In situ prepared reduced graphene oxide/CoO nanowires mutually-supporting porous structure with enhanced lithium storage performance, *Electrochim. Acta* 190 (2016) 276-284.
- [36] G. X. Gao, L. Yu, H. B. Wu, X. W. Lou, Hierarchical tubular structures constructed by carbon-coated α -Fe₂O₃ nanorods for highly reversible lithium storage, *Small* 10 (2014) 1741-1745.
- [37] X. F. Li, A. Dhanabalan, C. L. Wang, Enhanced electrochemical performance of porous NiO-Ni nanocomposite anode for lithium ion batteries, *J. Power. Sources* 196 (2011) 9625-9630.

- [38] L. W. Sun, Z. Zhou, P. W. Shen, Ni/C hierarchical nanostructures with Ni nanoparticles highly dispersed in N-containing carbon nanosheets: origin of Li storage capacity, *J. Phys. Chem. C* 116 (2012) 23974-23980.
- [39] L. W. Su, Y. R. Zhong, Z. Zhou, Role of transition metal nanoparticles in the extra lithium storage capacity of transition metal oxides: a case study of hierarchical core-shell $\text{Fe}_3\text{O}_4@\text{C}$ and $\text{Fe}@\text{C}$ microspheres, *J. Mater. Chem. A* 1 (2013), 15158-15166.
- [40] F. Wang, R. Robert, N. A. Chernova, N. Pereira, F. Omenya, F. Badway, X. Hua, M. Ruotolo, R. G. Zhang, L. J. Wu, V. Volkov, D. Su, B. Key, M. S. Whittingharn, C. P. Grey, G. G. Amatucci, Y. M. Zhu, J. Graetz, Conversion reaction mechanisms in lithium ion batteries: study of the binary metal fluoride electrodes, *J. Am. Chem. Soc.* 133 (2011), 18828-18836.
- [41] F. Wang, H. C. Yu, M. H. Chen, L. J. Wu, N. Pereira, K. Thornton, A. Van der Ven, Y. M. Zhu, G. G. Amatucci, J. Graetz, Tracking lithium transport and electrochemical reactions in nanoparticles, *Nat Commun* 3:1201 (2012).
- [42] L. J. Zhang, P. Hu, X. Y. Zhao, R. L. Tian, R. Q. Zou, D. G. Xia, Controllable synthesis of core-shell $\text{Co}@\text{CoO}$ nanocomposites with a superior performance as an anode material for lithium-ion batteries, *J. Mater. Chem.* 21 (2011) 18279-18283.
- [43] L. Armelao, D. Barreca, S. Gross, A. Martucci, M. Tieto, E. Tondello, Cobalt oxide-based films: sol-gel synthesis and characterization, *J. Non-Cryst. Solids* 293-295 (2001) 477-482.

- [44] H. A. E. Hagelin-Weaver, G. B. Hoflund, D. M. Minahan, G. N. Salaita, Electron energy loss spectroscopic investigation of Co metal, CoO, and Co₃O₄ before and after Ar⁺ bombardment, Appl. Surf. Sci. 235 (2004) 420-448.
- [45] A. E. Berkowitz, K. Takano, Exchange anisotropy-a review, J. Magn. Magn. Mater. 200 (1999) 552-570.
- [46] M. Verelst, T. O. Ely, C. Amiens, E. Snoeck, P. Lecante, A. Mosset, M. Respaud, J. M. Broto, B. Chaudret, Synthesis and characterization of CoO, Co₃O₄, and mixed Co/CoO nanoparticles, Chem. Mater. 11 (1999) 2702-2708.
- [47] J.-S. Do, C.-H. Weng, Electrochemical and charge/discharge properties of the synthesized cobalt oxide as anode material in Li-ion batteries, J. Power. Sources 159 (2006) 323-327.
- [48] Y. Z. Jiang, Y. Li, P. Zhou, S. L. Yu, W. P. Sun, S. X. Dou, Enhanced reaction kinetics and structure integrity of Ni/SnO₂ nanocluster toward high-performance lithium storage, ACS Appl. Mater. Interfaces 7 (2015) 26367-26373.
- [49] L. Zhan, S. Q. Wang, L. X. Ding, Z. Li, H. H. Wang, Binder-free Co-CoO_x nanowire arrays for lithium ion batteries with excellent rate capability and ultra-long cycle life, J Mater. Chem. A 3 (2015) 19711-19717.
- [50] S. Grugeon, S. Laruelle, L. Dupont, J.-M. Tarascon, An update on the reactivity of nanoparticles Co-based compounds towards Li, Solid State Sci. 5 (2003) 895-904.

- [51] A. Ponrouch, P. L. Taberna, P. Simon, M. R. Palacín, On the origin of the extra capacity at low potential in materials for Li batteries reacting through conversion reaction, *Electrochim. Acta*, 61 (2012) 13-18.
- [52] Y. Xiao , X. Wang , W. Wang , D. Zhao, H. M. Cao, Engineering hybrid between MnO and N-doped carbon to achieve exceptionally high capacity for lithium-ion battery anode, *ACS Appl. Mater. Interfaces* 6 (2014) 2051-2058.
- [53] W. Q. Zhang, X. N. Li, J. W. Liang, K. B. Tang, Y. C. Zhu, Y. T. Qian, One-step thermolysis synthesis of two-dimensional ultrafine Fe₃O₄ particles/carbon nanonetworks for high-performance lithium-ion batteries, *Nanoscale* 8 (2016) 4733-4741.
- [54] Z. T. Cui, S. G. Wang, Y. H. Zhang, M. H. Cao, High-performance lithium storage of Co₃O₄ achieved by constructing porous nanotube structure, *Electrochim. Acta*, 182 (2015) 507-515.
- [55] P. Balaya,, H. Li, L. Kienle, J. Maier, Fully reversible homogeneous and heterogeneous Li storage in RuO₂ with high capacity. *Adv. Funct. Mater.* 13(2003) 621-625.
- [56] Y. Mao , H. Duan , B. Xu , L. Zhang , Y. Hu , C. Zhao , Z. Wang , L. Chen, Y. Yang, Lithium storage in nitrogen-rich mesoporous carbon materials, *Energy Environ. Sci.* 5 (2012) 7950-7955.
- [57] P. Balaya , A. J. Bhattacharyya , J. Jamnik , Y. F. Zhukovskii , E. A. Kotomin, J. Maier, Nano-ionics in the context of lithium batteries, *J. Power Sources* 159 (2006) 171-178.

- [58] Y. Y. Hu, Z. G. Liu, K. W. Nam, O. J. Borkiewicz, J. Cheng, X. Hua, X. M. T. Dunstan, X. Q. Yu, K. M. Wiaderek, L. S. Du, K. W. Chapman, P. J. Chupas, X. Q. Yang, C. P. Grey, Origin of additional capacities in metal oxide lithium-ion battery electrodes, *Nat. Mater.* 12 (2013) 1130-1136.
- [59] S. Laruelle, S. Grugeon, P. Poizot, M. Dollé, L. Dupont, J.-M. Tarascon, On the origin of the extra electrochemical capacity displayed by MO/Li cells at low potential, *J. Electrochem. Soc.* 149 (2002) A627-A634.
- [60] Y. Wang, Z. W. Fu, Q. Z. Qin, A nanocrystalline Co_3O_4 thin film electrode for Li-ion batteries, *Thin Solid Films* 441 (2003) 19–24.
- [61] X. Q. Yu, Y. He, J. P. Sun, K. Tang, H. Li, L. Q. Chen, X. J. Huang, Nanocrystalline MnO thin film anode for lithium ion batteries with low overpotential, *Electrochem. Commun.* 11 (2009) 791–794.
- [62] S. Khamlich, Z.Y. Nurua, A. Belloc, M. Fabianec, J.K. Dangbegnon, N. Manyalac, M. Maazaa, Pulsed laser deposited Cr_2O_3 nanostructured thin film on graphene as anode material for alithium-ion batteries, *J. Alloys Comd.* 637 (2015) 219-225.
- [63] J. Jamnik, J. Maier, Nanocrystallinity effects in lithium battery materials Aspects of nano-ionics. Part IV, *Phys. Chem. Chem. Phys.* 5 (2003) 5215-5220.
- [64] Y. Xiao, C.W. Hu, M.H. Cao, High lithium storage capacity and rate capability achieved by mesoporous Co_3O_4 hierarchical nanobundles, *J. Power Sources* 247 (2014) 49-56.

[65] J. H. Kim, Y. C. Kang, Electrochemical properties of micron-sized, spherical, meso- and macro-porous Co_3O_4 and CoO -carbon composite powders prepared by a two-step spray drying process, *Nanoscale* 6 (2014) 4789-4795.

[66] Y. Ma, G. Ji, B. Ding, J. Y. Lee, Facile solvothermal synthesis of anatase TiO_2 microspheres with adjustable mesoporosity for the reversible storage of lithium ions, *J. Mater. Chem.* 22 (2012) 24380-24385.

Figures and captions:

Fig. 1 Structure and composition characterization of CoO-Co composite: (a) XRD patterns, (b) XPS spectrum, and (c) Magnetism hysteresis loops at 300 K.

Fig. 2 The high-resolution TEM image with inset showing SAED patterns of CoO-Co nanocomposite.

Fig. 3 The first five cyclic voltammetry curves of CoO-Co nanocomposite anode at a scan rate of 0.1 mV s^{-1} from 0.01 V to 3 V.

Fig. 4 (a) Cycling performance of CoO-Co nanocomposite and corresponding Coulombic efficiency at a specific current of 500 mA g⁻¹. (b) Discharge-charge profiles of CoO-Co based anode cycled between 0.01 V-3 V at a current of 500 mA g⁻¹.

Fig. 6 SEM images of CoO-Co anode before (a, c) and after (b, d) cycles.

Fig. 6 Cycling performance of CoO grown at 0.3 Pa and corresponding Columbic efficiency at a specific current of 500 mA g⁻¹.

Fig. 7 (a) Rate performance of CoO anode grown at 0.2 Pa and 0.3 Pa at various current densities from 500 mA g⁻¹ to 10000 mA g⁻¹, (b) Nyquist plots of CoO

anodes grown at 0.2 Pa and 0.3 Pa obtained by applying a sine wave with
amplitude of 5 mV from 100 kHz to 0.01 Hz.