***In Situ* Fabrication of Nano Porous NiO-Capped Ni₃P film as Anode for Li-Ion Battery with Different Lithiation Path and Significantly Enhanced Electrochemical Performance**

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Abstract

Nickel phosphide (Ni₃P) is a promising anode material for lithium-ion batteries owing to its high specific capacity, though significant improvement in its cycling stability is highly desired. Here we propose an effective and low-cost solution via a three-dimensional construction of porous NiO covered Ni₃P films over a substrate of Ni foam, through electroless plating of P-rich Ni₃P and subsequent *in situ* oxidation in air. The *in situ* oxidation of P-rich Ni₃P resulted in the formation of nano porous NiO capping layer. Remarkable enhancement in the cycling stability of such a composite anode was thus realized. The initial discharge capacity for a CR2016-type coin cell was as high as 920 mA h g⁻¹, and there was still a reversible capacity of 550 mA h g⁻¹ after 60 cycles at a current density of 38.8 mA g⁻¹. The presence of porous NiO capping layer changed the lithiation path and significantly improved the cycling performance. The decreased resistance in charge transport due to the existence of adequate channels for Li ions diffusion also enhanced rate performance. A pristine Ni₃P films was researched as a

comparison.

Keywords: nano porous NiO film; P-rich phosphide; nickel phosphide; lithium-ion battery

1. Introduction

Intense effort in developing high-capacity lithium batteries originates from the growing demand for portable electronic devices and the potential uses in electric vehicles of lithium batteries. At present, transition metal phosphides have attracted great attention as a novel anode material because of their higher gravimetric capacity compared with commercial graphite and lower polarization with respect to fluorides, oxides, and sulphides [1-10]. So far, numerous binary and ternary metal phosphides have been exploited as negative electrodes, e.g. MnP_4 , CoP_3 , ZnP_2 , Zn_3P_2 , InP , GaP , Cu_3P , VP , VP_2 , VP_4 , FeP , FeP_2 , and FeP_4 [11-23]. However, to date the application of phosphides in practical Li-ion batteries is still seriously impeded by the relatively large initial irreversible loss and poor capacity retention due to huge volume changes from anode reactions associated with the charging-discharging cycles [5, 24, 25]. The electrochemical conversion mechanism to **insert** Li^+ ions to a phosphide in the anode is [26, 27]:

Such a conversion reaction between Li^+ **and metal** phosphide M_xP_y would cause pronounced change in **phase composition**, and thus deteriorate the structural integrity of the anode material, which would result in loss of capacity and degrading cycling stability. Repeating conversion processes during charging-discharging would result in pulverization of the anode and finally destroy **of its initial structure** [28-31]. Additionally, some typical transition metal phosphides are rather compact in phase structures, which is the reason why these materials are resistive to environmental corrosion. However, the

dense packing in electrode structures is not helpful for fast lithiation / delithiation of the anode material, leading to low electrochemical response of the battery system.

Among the transition metal phosphides, Ni_3P reacts with Li^+ at an average voltage about 1 V and induces flat charge and discharge curves separated by about 0.4 V [29-31]. Great endeavor has been made in order to improve the electrochemical performance of the anode material based on Ni_3P powder. In particular, extensive efforts have been made by reducing the particle sizes of Ni_3P powders, in order to minimize structural damages in the materials during charging-discharging cycles. For example, it was shown that micrometer-scale Cu_3P powders fabricated by a solvothermal method had better cycling performance than that of coarser powders prepared by methods such as ball milling, high temperature sintering and thermal spraying [32, 33]. Hall and Trizio demonstrated that refining phosphide powders from the micrometer scale down to nanometer scale led to further improvement of structural stability of the phosphide anode [34-36]. While refining powders down to nanometer scale could improve the structural integrity effectively, a large irreversible loss from 2000 to 700 mA h g^{-1} in the first cycle was observed by Xu et al.[37], which was typical to previously reported nano-powders of other phosphide anode materials [38-40]. The formation of a solid electrolyte interface (SEI) is largely behind the remarkable capacity loss associated with nano-powders, wherein the large specific interfacial area could enhance SEI formation and enlarge loss in capacity during initial cycles. It was not surprising to find that the electrochemical stability of phosphide anodes could also be enhanced by coating Ni_3P nano-powder with conductive materials such as carbon materials [24, 25, 33], as such suitable coatings could help minimizing the structural instability of anode materials, together with decreased charge transfer impedance associated with the lithiation / delithiation process [41, 42]. It is, however, worth noting that it is nontrivial to coat nano-powders with well-controlled uniformity in terms of thickness and composition. It is therefore reasonable to envisage that the cycling stability of phosphide anode could be effectively

improved through a layered construction of the active material and suitable protective coatings. **Structural damage** in the phosphide could thus be minimized via decreased lithiation / delithiation depth or the layer thickness **in the active anode material**, and further structural stability could be provided from suitable coating on the top to allow reduced specific electrode/electrolyte interfacial area and spatial confinement of the active material below. The smaller specific interfacial area than that of the nano-powders is also considered **to be helpful to** alleviate capacity loss in the initial cycles due to pressed SEI formation [43].

In this work, we present a low-cost technique to construct layered phosphide / NiO structures over the cavity surfaces of foamed Ni. The active film of phosphide material was coated to a substrate of Ni foam using the well-established and low-cost electroless plating method [34]. A porous capping layer of nano-crystalline NiO film was then introduced over the surface of the Ni₃P film by *in situ* oxidation, on the basis that porous transition metal oxides such as CoO, NiO and CuO have been identified as stable materials during the electrochemical cycles [5-7, 22]. Such an oxide capped anode based on Ni₃P thin-film is shown, for the first time, to offer remarkable enhancement in cycling stability through highly improved structural stability. Compared to naked Ni₃P films, after 60 cycles, the discharge capacity of NiO capped Ni₃P is 3 times higher, which is much improved than the yields ever reported for Ni₃P. The new strategy provides us a cost-effective way, beyond carbon-shell structure, to improve the structure stability and cycling performance by a nano porous capping layer for lithium battery.

2. Experimental section

The Ni₃P phosphide film was coated on the surfaces of interconnected pores throughout substrates of foamed nickel plates (12 mm in diameter, 0.2 mm in thickness), using an electroless plating process conducted in a water bath. The aqueous plating solution consisted of NiSO₄·6H₂O (44 gL⁻¹), NaH₂PO₂·H₂O (24.4 gL⁻¹), citric acid monohydrate (16 gL⁻¹), NaAc (18 gL⁻¹), lactic acid (6 gL⁻¹) and tartaric acid (6 gL⁻¹). Before plating,

the foamed nickel substrates were subjected to ultrasonic cleaning sequentially in acetone, deionized water, and dilute hydrochloric acid, and then dried in vacuum. The electroless plating was conducted at 90°C for 20 minutes under constant magnetic stirring, with the PH value of electrolyte maintained at 3~4. The resultant phosphide films were typically of an amorphous structure.

The as-plated films were then annealed at 600°C for 30 minutes in argon gas and in air respectively, and cooled down to room temperature within the furnace. This resulted in two kinds of annealed **Ni₃P film samples**, porous NiO-capped Ni₃P film (PNCP) in air and naked Ni₃P **in argon gas**. The structure and surface morphology of the films thus obtained were characterized by X-ray diffraction (XRD, Rigaku Ultima IV) with the Cu K α radiation, and field-emission scanning electron microscopy (FE-SEM, Sirion-200) equipped with an energy disperse X-ray (EDX) spectroscopy system, respectively.

Electrochemical performance was investigated with a CR2016-type of two-electrode half cell, using lithium foil as the negative electrode. The electrolyte was made of 1 M LiPF₆ dissolved in ethylene carbonate (EC) and diethyl carbonate (DMC) with the volumetric EC / DMC ratio being 1:1. The separator was in the form of micro-porous film of polypropylene. The nickel foam coated with Ni₃P films annealed in either air or argon gas were used as the anode. The CR2016-type coin cells were assembled in a glove box filled with high-purity Ar (Mbraun-MBC-Q13-588, O₂ < 0.1 ppm, H₂O < 0.1 ppm). The galvanostatic charge-discharge tests were conducted on a LAND CT2001A battery testing system in the voltage range of 0.01 to 3.0V (versus Li / Li⁺) in the incubator with the constant temperature at 25 °C. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on an electrochemical workstation (PARSTAT 4000, at 25 °C). For the specific capacity evaluation, the net weight of Ni₃P layer was measure before and after plating of Ni₃P coating. For NiO-capped Ni₃P film, the total weight of NiO and Ni₃P was measured by using a microbalance with readability of 10 μ g (Mettler Toledo MS105, Switzerland). **When the**

capacity was determined, the error estimation has been taken into account. The capacity was measured for 3 times and the error bar was used for error estimations. And the average values were used for discussion.

3. Results and discussion

The as-plated film was in an amorphous state. Fig. 1a shows XRD patterns of as-deposited phosphide film. Only nickel peaks from the foamed Ni substrate are presented, which indicates an amorphous state of the as-deposited phosphide. Figs. 1(b) and 1(c) show the XRD patterns of the annealed phosphide in Ar gas and air, respectively. Except for the diffraction peaks from Ni substrate, after annealing in both atmosphere, the tetragonal structure of Ni_3P ($a=b=8.952 \text{ \AA}$, $c=4.338 \text{ \AA}$) was formed. The formation of an additional NiO phase in the latter was attributed to reaction with oxygen in air during annealing. It was reported that chemically reduced Ni can also exist in the electroless plated phosphide film as a minor phase [24, 34], though it will be shown later that this is not the case here owing to enrichment of P in the phosphide film.

Fig. 2(a) shows the overall morphology of the Ni foam, and Fig. 2(b) shows a largely smooth surface of the interconnected cavities in the Ni foam. Figs. 2(c - f) compare the morphology of coated Ni foam after annealing in Ar gas and air, respectively. It can be seen that, before electroless plating, the surface of the foamed Ni substrate consisted of equiaxed Ni grains of the size of about $10 \text{ }\mu\text{m}$. The surface was completely covered by the phosphide layer after plating. The electroless plated phosphide film consists of particles with the diameter of 100 nm and the surface is relatively compact (Figs. 2c and 2e). Meanwhile, Figs. 2(d, f) exhibited evidently different morphological features from the sample annealed in air. The surface morphology of the sample annealed in air shows a relatively porous structure, with some pores shown to go downward to the material below (Fig. 2f and Fig.3a in detail). And the porous structure is composed by 3 dimension interconnected fiber-like branches. The results from energy dispersive X-ray (EDX) spectroscopy for the Ni_3P layer proved that the atomic Ni / P ratio is about 2.4.

According to the XRD result, the phosphide pattern is in excellent agreement with the standard powder pattern for the Ni₃P phase. The film is therefore regarded as a P-rich Ni₃P phase. The high content of P can help lower the crystallization temperature of the amorphous phosphide film [40]. As indicated by eqn. (1), in a certain sense, the contents of P determine the charge–discharge capacity of the metal phosphides. The porous nature of the NiO capping layer was also clearly proved by surfacial elemental mapping. A typical selected area shown by a secondary electrons image in Fig.3b was analyzed concerning element distribution. Imaging with secondary electrons provides information about morphology and surface topography. The contrast is dominated by the so-called edge effect, which is also sensitive to the porous structure on the surface. Fig. 3 c and d proves the surface of the sample annealed in air consists mainly of Ni and O, indicating that the surface is covered by an oxide layer. The overlapped mapping of Ni and O distribution on the PNCP surface (Fig. 3c) doesn't show any colour contrast, and pores in the oxide are shown as dark spots. The porous surface covered the whole Ni₃P surface. The carbon was previously deposited on the surface to help diminish static electricity accumulation during SEM observation.

The typical cross section image of sample annealed in air, is shown in Fig. 4. The low-magnification inset in Fig. 4(a) shows a selected region around a tube-like cavity in the substrate Ni foam. The outer surface of Ni₃P coating is covered with a coarse thin layer of materials with lower atomic mass, i.e. the NiO formed during annealing in air. The Ni₃P film is about 1.3 μm in thickness. The elemental mapping (Fig.4 b~d) is supportive that the Ni₃P coating is covered by a much thinner NiO layer less than 100 nm in thickness, with the oxygen mapping corresponding to the NiO layer indicated in Fig. 4(a). An overall view for the inset in Fig.4(a) is shown in Fig. 4f. The homogeneous distribution of Ni and P in the phosphide films is attributable to their simultaneous formation by the redox reactions [24, 28, 44].

So that both elements could mix randomly at an atomic scale to form an amorphous film (Fig.1a). As was determined by the EDX quantification, the as-plated phosphide was rich in P element. During annealing in air, co-oxidation of both Ni and P occurred over the surface of the Ni₃P film and the formation of volatile P oxide accounted for the formation of nano-or micro-pores in the NiO film. The formation of P-rich amorphous Ni₃P layer contributed to void formation [45-47].

Fig.5a shows the galvanostatic charge/discharge response of the PNCP films, recorded in the potential range of 0.01 V to 3.0 V at a current density of 38.8 mA g⁻¹ (0.1 C). The initial discharge capacity was 920 mA h g⁻¹, and the retained capacity after the 10th cycle was still as high as 610 mA h g⁻¹, which was still two-third of the initial capacity. This is remarkably higher than what achieved in previous reports, which showed that the capacity retention for phosphide electrodes after the first cycle was never higher than 45%, even by compositing phosphide powder with carbon or by powder refining [34, 37-39]. The establishment of SEI mainly accounts for the high capacity loss in the initial cycles for nickel phosphide based anodes. The direct contact of transition metal phosphide with electrolyte will also cause the catalyzed decomposition of organic molecules. Both processes occurred at a low potential [48-51]. It was reported that for the NiO anode materials, the energy loss due to the SEI formation is relatively low [5-7, 11, 22]. In the present case, the presence of an oxide layer can diminish the energy loss in the initial cycles as an intermediate layer between active material and electrolyte. The capping NiO is also expected to offer mechanical reinforcement to hold the Ni₃P film a piece, while pores through the oxide can provide spatial allowance to accommodate volumetric expansion associated with the lithiation of the electrode.

Indeed, capacity loss for the Ni₃P film without a NiO capping layer is shown in Fig. 5b for comparison. For the naked Ni₃P film without NiO capping, nearly half capacity loss occurred in the second cycle. For PNCP (Fig. 5a), decay in the capacity was low after

the first cycle and even after 60 cycles the discharge capacity of 550 mA h g⁻¹, or 60% of the initial capacity, was still retained. Also, a broad plateau at the potential from 1.5 V to 1.0 V existed in the discharge curve for NiO-capped Ni₃P film, which corresponded to the successive phase transformation from Ni₃P to Li₃P through lithiation of the electrode [3, 37-39, 52]. During the delithiation scan, the anodic plateaus at the potential of about 2.2 V and 1.5 V are associated with the reformation of Ni₃P [37]. After 25 cycles, specific capacity of pure Ni₃P film decreased to less than 200 mA h g⁻¹. This confirms the fairly impressive benefit from utilizing a porous NiO capping layer in improving the cycling stability of the electrode.

Fig. 5a and b shows some difference in anodic and cathodic reactions, indicating that porous NiO film did change reaction path in the cycling [38, 39]. The lithium storage performance of Ni₃P–Ni arrays was characterized by cyclic voltammetry (CV) to identify the influence of porous NiO on the electrochemical reaction undergone by the Ni₃P. Fig.6 a and b shows CV curves of the PNCP and bare Ni₃P electrode in the 0.01-3 V versus Li / Li⁺ potential window at a scan rate of 0.05 mV s⁻¹. The cathodic and anodic peaks are corresponding well with the discharge-charge plateaus in Fig. 5. During the de-lithiation scan the anodic peak at the potential of about 2.3-2.4 V is associated with the re-formation of Ni₃P [31], which is similar for both electrodes. An additional anodic peak appeared in Fig.6 b, indicating Li⁺ extraction from different Li⁺ insertion products [2, 31]. The successive phase transformation upon lithium-ion insertion via crystalline Ni₃P to form Li₃P alloy occurred around the potential of 1.0 V [2, 31].. Accordingly, the electrode reaction of Ni₃P was expressed as:

The positive shift of cathodic reaction peaks can be observed by the presence of porous oxide layer (Fig.6 a and b). The formation of LiP, instead of Li₃P, would contribute to the reaction at the low potential ~ 0.73 V [31]. For the lithiation reaction to generate LiP, it delivers a low capacity of 130 mA h g⁻¹, which is the reason that naked Ni₃P

demonstrates a lower capacity. At the same time, the interval between anodic and cathodic peaks is suggested as the polarization of the electrode. Therefore, PNCP electrode shows the lower polarization as indicated in Fig. 6. The low polarization would improve cycling performance (Fig.7).

In Fig. 7, we compared the cycling performances of PNCP film and the naked Ni_3P film as electrodes. After 60 cycles, the PNCP film still delivered a capacity of 558 mA h g^{-1} , which is about 91% of the capacity in 2nd cycle and is remarkably more stable than the naked Ni_3P film. For the naked Ni_3P film, a continuing decay in the capacity led to a specific capacity as low as 147 mA h g^{-1} after 60 cycles. The coulombic efficiency was high for both PNCP and naked electrodes (filled data points). However, the PNCP electrode demonstrated a more stable coulombic efficiency. In previous literatures, the electrodeposited Ni_3P never demonstrated a stable capacity higher than this value within 60 cycles [31, 48- 50]. The fabrication of core-shell and other hybridizing structures can retain 450 mA h g^{-1} and 200 mA h g^{-1} within 50 cycles, respectively in [6 and 53]. By construction of $\text{C@Ni}_3\text{P/Ni/C}$ complicated structure, the energy loss within 60 cycles with respect to the 2nd cycle was **only more than** 30% [54, 55]. It is worth pointing out that electrodes made of compact NiO alone also suffers from rapid capacity decay during charging/discharging cycles, which is caused by severe pulverization associated to significant volumes changes from the lithiation/delithiation processes. It was observed that the construction of nano-porous material was an effective way to overcome this drawback for NiO material [56, 57]. For PNCP electrode, a decline near 60 cycles was observed. A comparison of CV curves at 2rd and 61st cycles (Fig.8) demonstrated an evident negative shift of cathode reaction potential, which enhanced the polarization of electrode.

It is also reasonable to postulate that the porous NiO would permit adequate infiltration of electrolyte to the underlining active phosphide layer for quick transport of Li^+ ions during charging-discharging cycles. The rate capabilities for the phosphide electrodes

with and without the porous NiO capping layer are compared in Fig. 9a. The capacities of PNCP film and Ni₃P film were 600 mA h g⁻¹ and 340 mA h g⁻¹ at the current density of 19.4 mA g⁻¹ (0.05C), respectively. When the current density increased to 388 mA g⁻¹ (1C), the respective capacity for the PNCP and Ni₃P electrodes dropped to about 360 mA h g⁻¹ and 130 mA h g⁻¹. Moreover, when the current density was dropped back to 19.4 mA g⁻¹ (0.05C), the loss in the capacity was reversely recovered back to about 580 mA h g⁻¹ for the electrode of the PNCP film, while the capacity for the naked Ni₃P electrode was recovered to a lesser extent, back to 220 mA h g⁻¹. Overall capacity retention was about 97% for the PNCP electrode and 65% for the naked phosphide film, respectively. The radical improvement in rate capability for the PNCP electrode is attributable to highly reduced damage in the electrode structure and the advantages of porous NiO layer in shortening depth for lithium insertion/extraction, together with shortcuts for electrolyte to access the phosphide material below. A comparison of two electrode surface SEM images after 100 cycles at 0.1 C. is shown as Fig.10. In Fig.10a, the exposure of Ni substrate was indicated by arrows, which proved the damage of Ni₃P during the cycling. For PNCP electrode, the surface was peeling-free. The beneficial effect of the porous NiO capping layer on Li⁺ transport and structural integrity was also supported by the results of electrochemical impedance spectroscopy (EIS), which revealed significantly lowered resistance in charge transport due to the existence of porous NiO. Fig. 9b shows the impedance plots for electrodes of PNCP and Ni₃P films, recorded from 0.01 Hz to 10 kHz. It is seen that the starting point of the impedance curve of Ni₃P films is not zero, implying existence of the additional resistance in the system. Compared with the plot for the naked Ni₃P film, the impedance plot for the PNCP film exhibits a smaller semicircle in the medium frequency region, suggesting a lower electron transfer resistance. This can be attributed to the combined effects such as good structural integrity, together with adequate porous channel for electrolyte to access the phosphide materials beneath the NiO capping.

4. Conclusions

A new low-cost approach has been developed in order to overcome the serious problem of large capacity decay of phosphide electrodes for Li ion batteries, via electroless plating of Ni_3P over Ni foam, followed by an annealing in air to induce a nano-porous layer of NiO, with the nickel foam acting as a current collector and the oxide capped phosphide as active electrode. The porous nano-crystalline NiO layer below 100 nm in thickness acts as a capping layer to the phosphide film beneath, which contributes to remarkable improvement of the cycling stability of composite electrode. Compared to naked Ni_3P films, an electrode made of porous NiO capped Ni_3P film was shown to enable remarkably reduced capacity loss, so that 60% of the initial high discharge capacity of 920 mA h g^{-1} was retained (550 mA h g^{-1}) after 60 cycles at a current density of 38.8 mA h g^{-1} . Based on the electrochemical measurement, it is speculated the porous nano-NiO capping layer enabled high cycling stability of the composite electrode, through (a) changing lithiation reaction path; (b) decreasing of impedance by allowing porous channels for adequate electrolyte access to promote Li^+ ion transport, and (c) offering spatial allowance to minimize local stress from volumetric changes during discharging-charging cycles. The overall benefit also resulted in improvement in cycling and rate performance.

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References

- [1] Hajizamani, M.; Alizadeh, A.; Ehsani, N.; Mirjani, M. A study on the effect of reducing agent content on the thickness of electroless Ni_3P deposits on B_4C nanoparticles. *Revue de Métallurgie*, 110 (2013)147-152.
- [2] Cruz, M.; Morales, J.; Sánchez, L.; Santos-Peña, J.; Martín, F. Electrochemical

properties of electrodeposited nicked phosphide thin films in lithium cells. *Journal of Power Sources*, 171 (2007) 870-878.

[3] Boyanov, S.; Gillot, F.; Monconduit, L. The electrochemical reactivity of the NiP_3 skutterudite-type phase with lithium. *Ionics*, 14 (2008)125-130.

[4] Chen, K.; Liu, C.; Whalley, D. C.; Hutt, D. A. Stability of Ni_3P and its effect on the interfacial reaction between electroless Ni-P and molten tin. *Electronics Materials and Packaging*, EMAP 2005. International Symposium on. IEEE, 2005, 107-111.

[5] Chen, W.; Gao, W.; He, Y. A novel electroless plating of Ni-P- TiO_2 nano-composite coatings. *Surface and Coatings Technology*, 204 (2010)2493-2498.

[6] Zhang, H.; Lu, Y.; Gu, C. D.; Wang, X. L.; Tu, J. P. Ionothermal synthesis and lithium storage performance of core/shell structured amorphous@ crystalline Ni-P nanoparticles. *CrystEngComm*, 14 (2012)7942-7950.

[7] Zhao, B.; Ke, X. K.; Bao, J. H.; Wang, C. L.; Dong, L.; Chen, Y. W.; Chen, H. L. Synthesis of flower-like NiO and effects of morphology on its catalytic properties. *The Journal of Physical Chemistry C*, 113 (2009)14440-14447.

[8] Lijie Wang, Xi Zhang, Hongqing Gao, Junhua Hu, Jing Mao, Changhao Liang, Peng Zhang, and Guosheng Shao. 3D CuO Network Supported TiO_2 Nanosheets with Applications for Energy Storage and Water Splitting. *Science of Advanced Materials*. 8(2016) 256–1262.

[9] Guoqin Cao, Lijie Wang, Zhenya Fu, Junhua Hu., Shaokang Guan, Caili Zhang, Ligu Wang, Shijie Zhu. Chemically anchoring of TiO_2 coating on OH-terminated $\text{Mg}_3(\text{PO}_3)_2$ surface and its influence on the in vitro degradation resistance of Mg-Zn-Ca alloy. *Applied Surface Science* 308 (2014) 38-42.

[10] Peiling Yuan, MengWei, ZhenyaFu, GuoshengShao, H. Tatsuoka, JunhuaHu. Reactive vapor deposition and electrochemical performance of nano-structured magnesium silicide on silicon and silicon carbide substrates. *Materials Science in Semiconductor Processing* 27(2014)873-876.

[11] Souza, D. C. S.; Pralong, V.; Jacobson, A. J.; Nazar, L. F. A reversible solid-state crystalline transformation in a metal phosphide induced by redox chemistry. *Science*, 296 (2002) 2012-2015.

[12] Pralong, V.; Souza, D. C. S.; Leung, K. T.; Nazar, L. F. Reversible lithium uptake by

CoP₃ at low potential: role of the anion. *Electrochemistry Communications*, 4 (2002) 516–520.

[13] Cabana, J.; Monconduit, L.; Larcher, D.; Palacin, M. R. Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions. *Advanced Materials*, 22 (2010) 170-192.

[14] Park, C. M.; Kim, J. H.; Kim, H.; Sohn, H. J. Li-alloy based anode materials for Li secondary batteries. *Chemical Society Reviews*, 39 (2010) 3115-3141.

[15] Hwang, H.; Kim, M. G.; Kim, Y.; Martin, S. W.; Cho, J. The electrochemical lithium reactions of monoclinic ZnP₂ material. *Journal of Materials Chemistry*, 17 (2007) 3161-3166.

[16] Bichat, M. P.; Pascal, J. L.; Gillot, F.; Favier, F. Electrochemical lithium insertion in Zn₃P₂ zinc phosphide. *Journal of Physics and Chemistry of Solids*, 67 (2006) 1233-1237.

[17] Kishore, M. S.; Varadaraju, U. V. Phosphides with zinc blende structure as anodes for lithium-ion batteries. *Journal of power sources*, 156 (2006) 594-597.

[18] Crosnier, O.; Nazar, L. F. Facile Reversible Displacement Reaction of Cu₃P with Lithium at Low Potential. *Electrochemical and solid-state letters*, 7 (2004) 187-189.

[19] Park, C. M.; Kim, Y. U.; Sohn, H. J. Topotactic Li insertion/extraction in hexagonal vanadium monophosphide. *Chemistry of Materials*, 21 (2009) 5566-5568.

[20] Gillot, F.; Ménétrier, M.; Bekaert, E.; Dupont, L.; Morcrette, M.; Monconduit, L.; Tarascon, J. M. Vanadium diphosphides as negative electrodes for secondary Li-ion batteries. *Journal of power sources*, 17(2007) 877-885.

[21] Kim, Y. U.; Cho, B. W.; Sohn, H. J. The Reaction Mechanism of Lithium Insertion in Vanadium Tetrphosphide A Possible Anode Material in Lithium-Ion Batteries. *Journal of The Electrochemical Society*, 152 (2005) 1475-1478.

[22] Boyanov, S.; Bernardi, J.; Gillot, F.; Dupont, L.; Womes, M.; Tarascon, J. M.; Monconduit, L.; Doublet, M. L. FeP: another attractive anode for the Li-ion battery enlisting a reversible two-step insertion/conversion process. *Chemistry of materials*, 18 (2006) 3531-3538.

[23] Boyanov, S.; Zitoun, D.; Ménétrier, M.; Jumas, J. C.; Womes, M.; Monconduit, L. Comparison of the electrochemical lithiation/delithiation mechanisms of FeP_x (x= 1, 2, 4) based electrodes in Li-ion batteries. *The Journal of Physical Chemistry C*, 113 (2009)

21441-21452.

- [24] Pan, J. H.; Huang, Q.; Koh, Z. Y.; Neo, D.; Wang, X. Z.; Wang, Q. Scalable synthesis of urchin-and flowerlike hierarchical NiO microspheres and their electrochemical property for lithium storage. *ACS applied materials & interfaces*, 5 (2013) 6292-6299.
- [25] Xiang, J. Y.; Tu, J. P.; Wang, X. L.; Huang, X. H.; Yuan, Y. F.; Xia, X. H.; Zeng, Z. Y. Electrochemical performances of nanostructured Ni₃P–Ni films electrodeposited on nickel foam substrate. *Journal of Power Sources*, 185 (2008) 519-525.
- [26] Villevieille, C.; Robert, F.; Taberna, P. L.; Bazin, L.; Simon, P.; Monconduit, L. The good reactivity of lithium with nanostructured copper phosphide. *Journal of Materials Chemistry*, 18 (2008) 5956-5960.
- [27] Feng, Y.; Zhang, H.; Mu, Y.; Li, W.; Sun, J.; Wu, K.; Wang, Y. Monodisperse Sandwich-Like Coupled Quasi-Graphene Sheets Encapsulating Ni₂P Nanoparticles for Enhanced Lithium-Ion Batteries. *Chemistry-A European Journal*, 21 (2015) 9229-9235.
- [28] Park, S. J.; Jang, Y. S. X-ray diffraction and X-ray photoelectron spectroscopy studies of Ni–P deposited onto carbon fiber surfaces: impact properties of a carbon-fiber-reinforced matrix. *Journal of colloid and interface science*, 263 (2003) 170-176.
- [29] Lu, Y.; Tu, J. P.; Gu, C. D.; Wang, X. L.; Mao, S. X. In situ growth and electrochemical characterization versus lithium of a core/shell-structured Ni₂P@C nanocomposite synthesized by a facile organic-phase strategy. *Journal of Materials Chemistry*, 21 (2011) 17988-17997.
- [30] Jordanov, N.; Wondraczek, L.; Gutzow, I. Thermodynamic properties of vitreous electrodes in a Ni/NiP glass-crystal Galvanic cell. *Journal of Non-Crystalline Solids*, 382 (2013) 125-132.
- [31] Liu, S.; Feng, J.; Bian, X.; Liu, J.; Xu, H. Electroless deposition of Ni₃P–Ni arrays on 3-D nickel foam as a high performance anode for lithium-ion batteries. *RSC Advances*, 5 (2015) 60870-60875.
- [32] Qiu, M. C.; Yang, L. W.; Qi, X.; Li, J.; Zhong, J. X. Fabrication of ordered NiO coated Si nanowire array films as electrodes for a high performance lithium ion battery. *ACS applied materials & interfaces*, 2 (2010) 3614-3618.

- [33] Liu, T.; Zhao, L.; Wang, D.; Zhu, J.; Wang, B.; Guo, C. Corrosion resistance of nickel foam modified with electroless Ni–P alloy as positive current collector in a lithium ion battery. *RSC Advances*, 3 (2013) 25648-25651.
- [34] Hall, J. W.; Membreno, N.; Wu, J.; Celio, H.; Jones, R. A.; Stevenson, K. J. Low-temperature synthesis of amorphous FeP₂ and its use as anodes for Li ion batteries. *Journal of the American Chemical Society*, 134 (2012) 5532-5535.
- [35] Lu, Y.; Tu, J. P.; Xiong, Q. Q.; Qiao, Y. Q.; Wang, X. L.; Gu, C. D.; Mao, S. X. Synthesis of dinickel phosphide (Ni₂P) for fast lithium-ion transportation: a new class of nanowires with exceptionally improved electrochemical performance as a negative electrode. *RSC Advances*, 2 (2012) 3430-3436.
- [36] De Trizio, L.; Figuerola, A.; Manna, L.; Genovese, A.; George, C.; Brescia, R.; Saghiş, Z.; Simonutti, R.; Huis, M. V.; Falqui, A. Size-Tunable, Hexagonal Plate-like Cu₃P and Janus-like Cu–Cu₃P Nanocrystals. *ACS nano*, 6 (2011) 32-41.
- [37] Liang, Z.; Huo, R.; Yin, S.; Zhang, F.; Xu, S. Eco-efficient synthesis route of carbon-encapsulated transition metal phosphide with improved cycle stability for lithium-ion batteries. *Journal of Materials Chemistry A*, 2 (2014) 921-925.
- [38] Liu, S.; Feng, J.; Bian, X.; Liu, J.; Xu, H. Electroless deposition of Ni₃P–Ni arrays on 3-D nickel foam as a high performance anode for lithium-ion batteries. *RSC Advances*, 5 (2015) 60870-60875.
- [39] Cruz, M.; Morales, J.; Sánchez, L.; Santos-Peña, J.; Martín, F. Electrochemical properties of electrodeposited nicked phosphide thin films in lithium cells. *Journal of Power Sources*, 71 (2007) 870-878.
- [40] Hu, Y.; Yang, L.; Shi, C.; Tang, W. Microstructural evolution and phase transformation kinetics of pulse-electroplated Ni-Cu-P alloy film during annealing. *Materials Chemistry and Physics*, 141 (2013) 944-950.
- [41] Chuanshuai Li, Shimin Hu, Lei Yang, Jiajie Fan, Zhiqiang Yao, Yiqiang Zhang, Guosheng Shao, and Junhua Hu. Light-Induced Ion Rectification in Zigzag Nanochannels. *Chem. Asian J.* 10(2015)2733-2737.
- [42] Peng Zhang, Lijie Wang, Xi Zhang, Changlu Shao, Junhua Hu, Guosheng Shao. SnO₂-core carbon-shell composite nanotubes with enhanced photocurrent and photocatalytic performance. *Applied Catalysis B: Environmental* 166-167 (2015)

193-201.

[43] Peng Zhang, Lijie Wang, Xi Zhang, Junhua Hu, Guosheng Shao. Three-dimensional Porous Networks of Ultra-long Electrospun SnO₂ Nanotubes with High Photocatalytic Performance. *Nano-Micro Lett.* 7 (2015) 86-95.

[44] Makkar, P.; Agarwala, R. C.; Agarwala, V. Chemical synthesis of TiO₂ nanoparticles and their inclusion in Ni-P electroless coatings. *Ceramics International*, 39 (2013) 9003-9008.

[45]Heriberto Pfeiffer, Franck Tancrét, Thierry Brousse. Synthesis, characterization and thermal stability of Ni₃P coatings on nickel. *Materials Chemistry and Physics* 92 (2005) 534-539.

[46] W. Kai a,Y.H. Wua, I.F. Jen, T.H. Ho, H.H. Hsieh. Air-oxidation of a Pd₄₀Ni₄₀P₂₀ bulk glassy alloy at 250-420°C. *J. Alloys and Compounds* 586 (2014) S24-S30

[47] Shuna Zhang, Shujuan Zhang, Limin Song, Xiaoqing Wu, Sheng Fang. Three-dimensional interconnected nickel phosphide networks with hollow microstructures and desulfurization performance. *Materials Research Bulletin* 53 (2014) 158-162.

[48] J.Y. Xiang, J.P. Tu, X.L. Wang, X.H. Huang, Y.F. Yuan, X.H. Xia, Z.Y. Zeng. Electrochemical performances of nanostructured Ni₃P–Ni films electrodeposited on nickel foam substrate *Journal of Power Sources* 185 (2008) 519–525

[49] Manuel Cruz, Julián Morales, Luis Sánchez, Jesús Santos-Peña, Francisco Martín. Electrochemical properties of electrodeposited nicked phosphide thin films in lithium cells. *Journal of Power Sources* 171 (2007) 870–878.

[50] J.Y. Xiang, X.L. Wang, J. Zhong, D. Zhang, J.P. Tu. Enhanced rate capability of multi-layered ordered porous nickel phosphide film as anode for lithium ion batteries. *Journal of Power Sources* 196 (2011) 379–385

[51] Cai, G. F.; Gu, C. D.; Zhang, J.; Liu, P. C.; Wang, X. L.; You, Y. H.; Tu, J. P. Ultra fast electrochromic switching of nanostructured NiO films electrodeposited from choline chloride-based ionic liquid. *Electrochimica Acta*, 87 (2013) 341-347.

[52] F.Gillot, S.Boyanov, L.Dupont, M.L. Doublet, M.Morcrette, L. Monconduit, J.M. Tarascon. Electrochemical reactivity and design of NiP₂ negative electrode for secondary Li ion battery. *Chem. Mater.* 17(2005)6327-6337.

- [53] S. Carencu, C. Surcin, M. Morcrette, D. Larcher, N. Mézailles, C. Boissière, C. Sanchez. Improving the Li-Electrochemical Properties of Monodisperse Ni₂P Nanoparticles by Self-Generated Carbon Coating. *Chem. Mater.* (24)2012688–697.
- [54] Yi Lu, Xiuli Wang, Yongjin Mai, Jiayuan Xiang, Heng Zhang, Lu Li, Changdong Gu, Jiangping Tu, Scott X. Mao. Ni₂P/Graphene Sheets as Anode Materials with Enhanced Electrochemical Properties versus Lithium. *J. Phys. Chem. C* 116(2012)22217-22225.
- [55] Zhongqiang Liang, Ruijie Huo, Suhong Yin, Fazhi Zhang and Sailong Xu. Eco-efficient synthesis route of carbon encapsulated transition metal phosphide with improved cycle stability for lithium-ion batteries. *J. Mater. Chem. A*, 2(2014)921-925.
- [56] Huang, X. H.; Zhang, P.; Wu, J. B.; Lin, Y.; Guo, R. Q. Porous NiO/graphene hybrid film as anode for lithium ion batteries. *Materials Letters*, 153 (2015)102-105.
- [57] Pan, J. H.; Huang, Q.; Koh, Z. Y.; Neo, D.; Wang, X. Z.; Wang, Q. Scalable synthesis of urchin-and flowerlike hierarchical NiO microspheres and their electrochemical property for lithium storage. *ACS applied materials & interfaces*. 5 (2013) 6292-6299.

Figure caption

Fig.1. XRD patterns from (a) as-plated sample, (b) sample annealed in Ar, and (c) sample annealed in air.

Fig.2. Secondary electron SEM images from: (a, b) uncoated Ni foam with higher magnification showing smooth surface of the interconnected cavities (b); (c, e) sample annealed in Ar; (d, f) sample annealed in air. Note the highly rough surface with the existence of penetrating pores.

Fig.3 (a) SEM image for the porous surface of the PNCP film. (b) Secondary electron image of the PNCP surface and (c) Overlapped EDS elemental mapping of PNCP

surface, including Ni, P and C. (d) O mapping image generated from O *kα1*

Fig.4 Cross-section SEM image and EDX elemental mapping from the sample annealed in air: (a) back-scattered image, wherein the surface NiO oxide layer is indicated by a curved arrowhead. The inset in (a) is the selected area showing the cross-section of a tube-like cavity in the Ni foam. (b - d) corresponding elemental mapping of P, O, and Ni. (e) Overlapped elemental maps of Ni, P and O. (f) The external surface of the Ni tube is covered by NiO @ Ni₃P.

Fig. 5. Discharge-charge curves ranging from 0.01 to 3.0 V at the current density of 38.8 mA g⁻¹: (a) PNCP electrode; (b) naked Ni₃P electrode.

Fig.6 Initial CV curves of (a) PNCP and (b) Ni₃P. Some peaks were indicated by arrows.

Fig.7 Corresponding cycling performance and columbic efficiency for NiO capping film and naked Ni₃P film as the anode. The error estimation was demonstrated by error bars.

Fig.8 CV curves of PNCP at 2nd and 61st cycles.

Fig.9. (a) Rate capacities of PNCP and Ni₃P film at different current densities; The capacity was shown with error bars. (b) Nyquist plots for Ni₃P and PNCP films for the first lithiation process.

Fig.10 A SEM images comparison of two electrode surface after 100 cycles at 0.1 C. (a) Ni₃P and (b) PNCP. In Ni₃P, the exposure of Ni substrate, caused by the electrode damage was indicated by arrows and dotted oval.

Figure(s)

Fig.1.

Fig.2.

Fig.3

Fig.4

Fig. 5.

Fig.6

Fig.7

Fig.8

Fig.9

Fig.10