Electrochemical Na-Insertion/Extraction Property of Ni-Coated Black Phosphorus Prepared by an Electroless Deposition Method

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Supporting Information

ABSTRACT: Electrical conductivity is one of the properties required for an active material, and it is extremely essential to exert its potential. In the present study, the strategy of coating a metal at a single particle level by an electroless deposition method was applied to enhance the cycling performance of phosphorus-based negative electrodes for Na-ion batteries. The deposition morphology and composition of the Ni coating layer were characterized by field-emission scanning electron microscopy, scanning transmission electron microscopy, and X-ray diffraction. In the 5 wt % Ni coating, an amorphous Ni layer of several nanometers thickness was homogeneously formed on the phosphorus surface, whereas a shell layer having a 200 nm thickness was formed in the order of Ni12P9, NiP2, NiP, and metallic Ni from the surface toward the center in the 30 wt % Ni coating. Electrochemical impedance spectroscopic measurements clarified that the good electron transport proceeded throughout the developed conduction pathway to promote the phase transition to trisodium phosphide (Na3P), leading to a high theoretical capacity for phosphorus; the as-prepared black phosphorus showed only a reversible capacity of 140 mA h g−1 at the 60th cycle, whereas the 30 wt % Ni-coated composite delivered a relatively high capacity of 780 mA h g(P)−1. In addition, the expansion ratio of the electrode after the 30th desodiation was the lowest among the three kinds of electrodes. By contrast, cracks and exfoliation of the active material layer from the current collector were confirmed in the as-prepared black phosphorus. These results demonstrate that the upgraded performance accomplished using the 30 wt % Ni-coated composite with the Ni/Ni–P layer is due to the synergetic effects of the electron conduction channel and a buffer matrix against a large volumetric change (~400%) in phosphorus during the charge–discharge reactions.

INTRODUCTION

Toward the realization of a low-carbon society, Li-ion batteries (LIBs) have been not only used as power supplies for electric vehicles but also connected to smart grids. The worldwide popularization and rising demand for LIBs, however, require serious situations to be solved, such as the depletion of Li resources.1,2 As one answer to the problem, the development of new rechargeable batteries is eagerly anticipated. Na-ion batteries are in the spotlight because of their low cost and the high natural abundance of Na, and these batteries utilize the same system as LIBs from the viewpoint that the host materials absorb/release monovalent alkali-metal ions. To handle the serious situations to be solved, such as the depletion of Li resources, Na-ion batteries have been not only used as power supplies for electric vehicles but also connected to smart grids. The worldwide popularization and rising demand for LIBs, however, require serious situations to be solved, such as the depletion of Li resources.1,2 As one answer to the problem, the development of new rechargeable batteries is eagerly anticipated. Na-ion batteries are in the spotlight because of their low cost and the high natural abundance of Na, and these batteries utilize the same system as LIBs from the viewpoint that the host materials absorb/release monovalent alkali-metal ions. To handle the rapidly growing demand for applications in large-scale systems, advanced performances, such as high capacity and long cycle life, are required in host materials. With regard to the negative electrode materials, the development is focused on group 14 and group 15 elements, with the exception of nitrogen (N) and arsenic (As).1–11 In particular, tin (Sn)12–15 and phosphorus (P)16–20 have attracted much attention as alternatives to carbon-based materials,27–30 which show a reversible capacity of ~300 mA h g−1. Among the allotropes of phosphorus, red and black phosphorus can electrochemically react with Na to form a binary alloy.16,31 The formation of the most Na-rich phase, that is, the transformation of phosphorus to trisodium phosphide (Na3P), leads to a high theoretical capacity of 2596 mA h g−1, which is 10 times greater than the reversible capacity obtained from hard carbon.16,32 There is, however, a critical issue concerning the poor cycling performance. Because of the large size of the Na-ion (Shannon’s ionic radius: 1.02 Å), the volume of phosphorus expands and contracts by ca. 400% during the sodiation and desodiation reactions,33 which causes electrical isolation that is involved in the pulverization and peeling of the active material layer from the current collector. This is the remaining barrier to achieving a high electrode performance in phosphorus-based materials. In addition, phosphorus has an insufficient conductivity, which decreases the utilization of an active material. The use of a metal phosphide (M3P) is effective to improve the cycling performance of phosphorus-based electrodes by the synergetic effect.33 For instance, Sn4P3 undergoes a phase separation in the first...
cycle to form metallic Sn and phosphorus, in which Sn complements the poor electronic conductivity of phosphorus and the electrochemically formed Na–P acts as a shielding matrix against the aggregation of Sn.34–36 On the other hand, Li et al. reported that a favorable cycling performance was achieved in mechanically prepared CuP2.38 They demonstrated that CuP2 undergoes a phase separation to form elemental phosphorus and metallic Cu, and that, the resulting dispersed Cu nanoparticles serve as highly conductive electronic channels to enable fast electrochemical sodiation of phosphorus. In addition, Moncoutié et al. clarified that the charge–discharge of NiP, proceeds together with a conversion reaction to show an initial reversible capacity of 1022 mA h g⁻¹ and a good cycling performance with negligible capacity fading over 15 cycles (loss of 15%).39 This is also probably because of the enhanced electrical conductivity granted by the transition metal and even the buffer effect to the stress induced by the significantly large phosphorus volume change during the sodiation/desodiation reactions. Thus, the electrical conductivity of the active materials is a pre-eminent important key factor to improve the electrode performance. In fact, when electrons move from a current collector to an active material on the side close to a counter electrode, they are following electron transfers at the interfaces (Figure S1, Supporting Information): (i) between a current collector and an active material, (ii) between the active materials, and (iii) between a conductive additive and an active material. These transfer paths inevitably include the conduction in the active materials, that is, the electrical conductivity strongly affects the electrode performance. However, the application of such a transition metal phosphate imposes a limitation on the substantive capacity because the phosphorus content becomes relatively low. In the present study, we therefore attempted to coat the phosphorus powder with Ni on a single particle level by electroless deposition as a method of imparting electrical conductivity to enhance the cycling performance of phosphorus-based electrodes. Herein, we discuss the influence of the composition and deposition morphology on the electrochemical Na-insertion/ extraction properties.

### EXPERIMENTAL SECTION

**Synthesis.** Black phosphorus was prepared by the mechanical milling (MM) method using a high-energy planetary ball mill (Classic Line P-6, FRITSCH) in an argon atmosphere. Red phosphorus powder (Sigma-Aldrich, 97%) was used as the starting material and was placed in a stainless steel pot with five stainless steel balls (diameter: 15 mm). The weight ratio of the balls to the red phosphorus powder was set to 30:1. The MM time and rotation speed were 30 h and 380 rpm (6.33 Hz), respectively. Ni-coated phosphorus was synthesized by electroless deposition according to the following steps, including pretreatments. (1) Sensitization: black phosphorus powder (5 g L⁻¹) was immersed in 4.4 × 10⁻⁴ mol dm⁻³ (M) SnCl₂·2H₂O + 0.12 M HCl solution to adsorb Sn⁺⁺ on the particles. (2) Activation: Sn-adsorbed phosphorus was added to a solution of 5.6 × 10⁻⁴ M PdCl₂ + 0.12 M HCl, where Pd catalytic nuclei were formed on the particle by the displacement of Sn. In both the pretreatments, the solution temperature and processing time were 25 °C and 30 min, respectively. (3) Metallization (electroless deposition of Ni): 4.8 × 10⁻⁵ M hydrazine monohydrate (N₂H₄·H₂O) as the reducing agent was dripped into an aqueous solution containing 5.6 × 10⁻⁴ M Ni(OOCCH₃)₂·4H₂O as the Ni source, 1.6 × 10⁻⁴ M ethylenediamine-N₃N₇N₉N₇-tetraacetic acid (EDTA-2Na), 4.8 × 10⁻³ M lactic acid [CH₃CH(OH)-COOH] as the complexing agent, and Pd-activated phosphorus powder (1.0 g L⁻¹) under agitation using a magnetic stirrer. After stirring at 80 °C for 60 min, the suspension was filtered and washed with deionized water. The washed precipitate was dried under vacuum at 80 °C for 1 h to obtain Ni-coated black phosphorus as the final product. The above conditions correspond to 5 wt % Ni deposition; therefore, the concentration of the respective reagents must be increased with respect to the amount of Ni.

**Characterization.** The Ni content was determined by wavelength-dispersive X-ray fluorescence spectroscopy (WDS-XRF; ZSX Primus II, Rigaku). X-ray diffraction (XRD; SmartLab, Rigaku) with Cu Ka radiation and Raman microscopy system (TS6400; HORIBA, Ltd.) using the S32 nm line of a Nd:YAG laser were applied to identify the crystal structures of the samples. Elemental analysis was conducted by X-ray photoelectron spectroscopy (XPS; PHI Quantera II, ULVAC-PHI, Inc.) with an X-ray (monochromatic radiation Al Kα) beam diameter of 100 μm operated at 25 W. XPS spectra were calibrated using the binding energy of hydrocarbon (C–C, C–H groups) at 284.6 eV. The Ni-deposition morphology on black phosphorus was observed by field emission scanning electron microscopy (FE-SEM; JSM-7000F, JEOL Co., Ltd.) accompanied by energy-dispersive spectroscopy (EDS) and scanning transmission electron microscopy (STEM; HD2300A, Hitachi).

**Electrochemical Measurements.** The Ni-coated phosphorus powder (50 wt %) as the active material was mixed with acetylene black (AB, 30 wt %), carboxymethyl cellulose (CMC, 15 wt %, Mw: 90 000), and styrene butadiene rubber (SBR, 5 wt %). The resulting slurry was uniformly cast onto a Cu foil (18 μm thickness) using a doctor blade and then dried at 80 °C for 3 h under vacuum. The mass loading of the active material was approximately 0.5–0.8 mg cm⁻². 2032-Type coin cells consisting of the as-prepared electrode, Na foil (99.90%; Rare Metallic) as the counter electrode, an electrolyte, and a glass fiber filter (Whatman GF/A) as the separator were assembled in an argon-filled glovebox (dew point below −85 °C). The electrolyte solution consisted of 1.0 M sodium hexafluorophosphate (NaPF₆) dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 50/50, with or without 5 vol % fluoroethylene carbonate (FEC; Kanto Denka Kogyo Co., Ltd.). Galvanostatic charge–discharge tests were carried out in the voltage range of 0.005–1.500 V (vs Na/Na⁺) at 25 °C, and the current density was set to 260 mA g⁻¹ (0.1 C). Electrochemical impedance spectroscopy (EIS) measurement was performed using an [electrodeelectrolytelelectrode] symmetric cell in the frequency range of 100 kHz–10 mHz with an amplitude of 5 mV at 25 °C.60 First, in separate cells, two identical electrodes including an active material with the same loading mass were charged (sodiated) up to 0.005 V (vs Na/Na⁺) at 0.1 C and were then removed from the cells with the separators. The two negative electrode sheets were placed face-to-face in a fresh cell where the voltage was maintained within ±10 μV.

### RESULTS AND DISCUSSION

Black phosphorus as a base material was prepared from red phosphorus by mechanical milling. Among the allotropes of phosphorus, black phosphorus is nonflammable compared with red phosphorus and is insoluble in solvents. In addition, black
phosphorus has better electrical conductivity than red phosphorus. Thus, we employed phosphorus as the base material. The XRD patterns of the samples reveal that red phosphorus with a polymeric structure in which P4 tetrahedra are joined to each other by covalent bonds is completely transformed to black phosphorus with a layered two-dimensional structure after the MM process for 10 h (Figure S2, Supporting Information). The Raman spectra of red phosphorus milled for 10 h show bands that originate from one out-of-plane mode (A1g) and two in-plane modes (B2g and A2g) of black phosphorus at 360, 431, and 460 cm−1, which is in agreement with the XRD results (Figure S3, Supporting Information). As far as the condition (rotation speed: 380 rpm) is concerned, the black phosphorus phase is formed after 10 h; there is no significant change in the crystallinity, and only the grain size changed after the subsequent treatment. We selected the 30 h-milled phosphorus as the raw material and covered the phosphorus with Ni to the amount of 5, 10, 20, and 30 wt % by electroless deposition. In general, the amount of deposited metal is controlled by the treatment time. In this work, the content of Ni in the composite samples is the same as the amount of Ni(OOCCH3)2·4H2O (Ni sources) in the electroless deposition bath. That is, we added the Ni source by the required amount. After the addition of the reducing agent, the treatment time was set to 60 min so as to completely deposit. The actual contents of Ni determined by WDS analysis are 8, 14, 25, and 32 wt %. Figure 1 compares the Raman spectra and XRD patterns collected from the synthesized active materials with Ni amounts ranging from 0 to 30 wt %. The intensities of black phosphorus Raman bands are reduced with increasing Ni amounts. In other words, the coating layer formed on the phosphorus likely grew thicker while maintaining the core structure. No peaks were observed in the XRD patterns, with the exception of phosphorus up to a Ni coating of 10 wt %, which suggests that amorphous Ni was deposited onto the phosphorus surface. Meanwhile, with coatings of 20 wt % or more, peaks assigned to NiP3, NiP2, and Ni12P5 appeared, and the peak intensities for the compounds became strong with increasing Ni contents. The Ni−P atomic ratio of NiP3, NiP2, and Ni12P5 are 0.33, 0.5, and 2.4, respectively. In view of these results, we inferred that Ni diffuses through the surface inside of phosphorus to form Ni−P compounds in the order of Ni12P5, NiP2, and NiP3 from the surface toward the center. That is, a Ni-rich phase should be present at the outermost surface. The chemical species near the particle surface was analyzed using XPS with a monochromatic Al Kα X-ray source. Figure 2 shows the P 2p and Ni 2p core level spectra obtained from the Ni-coated phosphorus composite. The P 2p spectra consist of
three main components and an additional shouldker. Clear peaks are confirmed at 129.2 and 129.9 eV regardless of the electroless deposition treatment, and the peaks correspond to elemental phosphorus (P₀). The Ni−P layer, as a shell, likely became thicker because the signal intensity of phosphorus gradually diminished with increasing Ni content. The peak centered at 134.4 eV in the spectra of pristine phosphorus comes from a pentoxide such as P₄O₁₀ (P⁵⁺). Phosphorus has various valencies in its intermediate oxides; signals from 131 to 136 eV indicate the existence of phosphorus oxides, and the valence (x) can change from P³⁺ to P⁵⁺ (x < 5). The binding energy of 133.8 eV is attributed to the O−P=O bond with an oxidation state of P⁴⁺ (i.e., P₄O₆). The weak peak observed at the lower binding energy is due to the P−O−P bond (P³⁺) of P₄O₁₀. The shoulder at around 130 eV that appears for 20 and 30 wt % Ni-coated samples indicates the presence of Ni₁₂P₃, which is expected to be a component positioned at the surface of the Ni−P shell layer. The signature of Ni₁₂P₃ is shown not only in the P 2p spectra but also in the Ni 2p spectra. We can clearly confirm a peak at 853 eV associated with metallic Ni (Ni⁰), although no diffraction pattern derived from it was detected, which means that the deposited Ni on the phosphorus surface is in an amorphous state and has a thickness of several angstroms to several nanometers. Also in the 5 and 10 wt % Ni-coated composites, a slight signal associated with metallic Ni was observed. The appearance of a Ni-rich phase, such as Ni₁₂P₃ and metallic Ni, supports the above inference. However, the strong peak at 856.5 eV only appears with satellite peaks located at approximately 862 eV, with the electroless deposition of Ni. The signals originate from the Ni²⁺ species, such as NiO and Ni−P compounds, and NiO was probably formed owing to the reduction of P₄O₁₀ by the deposited metallic Ni. The decreasing oxygen concentration of phosphorus oxide as the amount of Ni coating increases also provides evidence for this. Given the results obtained from the XRD and XPS studies, the shell layers surrounding the core phosphorus are considered to be composed of amorphous Ni with some oxide, as far as Ni content is 10 wt %; however, the shell is composed of Ni₁₂P₅, NiP₂, and NiP₃ layers from the surface toward the center for coatings of 20 wt % or more. The results of the XPS depth profile of P 2p and Ni 2p regions obtained after different Ar-ion sputtering times strongly support the core−shell structure (Figure S4, Supporting Information). Part of the metallic Ni
remained, which as it is and partially resulted in NiO by the reduction of phosphorus oxide at the outermost surface.

Figure 3 displays the FE-SEM images and the corresponding EDS mapping results of the composite particles with Ni amounts of 5 and 30 wt %; the EDS mapping image of Ni Kα overlaps with that of P Kα, and the intensity of the X-ray fluorescence is homogeneously distributed; thus, α-Ni and Ni/P layers uniformly cover the phosphorus. At 10 and 20 wt % Ni deposition, uniform coatings are also successfully accomplished by electroless deposition, including sensitization and activation treatments (Figure S5, Supporting Information). STEM observations were conducted to examine the crystallinity and thickness of the shell layers in detail. Clear lattice fringes (with a d-spacing of 3.36 Å) are attributed to the (021) lattice plane of black phosphorus with an orthorhombic system (space group: Cmca/ICSD no. 01-073-1358) are confirmed in the highly magnified image for the 5 wt % Ni-coated sample (Figure 4a). The STEM and TEM analyses of the amorphous samples show a bright-field image that generally darkens when the product thickness and density increase. No lattice fringes are identified in the STEM images of 5 wt % Ni-coated phosphorus, which shows that the layer is still amorphous and is in good agreement with the XRD results. Considering these results, the shell layer is shown in the white parts, and the thickness is about 2 nm. By contrast, the thickness appears to be at least 60 nm for the 30 wt % Ni-coated sample; however, it is difficult to distinguish the contrasting density (Figure 4b). A focused ion beam (FIB) was applied to fabricate the cross-sectional surface of the composite particles. The particles were buried under a colloidal graphite powder in advance to protect against damage induced by the Ga ion of the FIB. Figure 4c shows a cross-sectional backscattered electron image of the 30 wt % Ni-coated phosphorus particle. The brightness of the image depends on the average atomic number and is useful to obtain compositional information. We can confirm that the shell layer has a coating thickness of 100–200 nm, as indicated by the bright region. Thus, from the STEM and FIB-SEM analyses (Figure S6, Supporting Information), the thickness of the Ni/Ni–P layer with the mixed phase is consequently revealed to include α-Ni, Ni12P3, NiP2, and NiP3, which is at least 40 nm but less than 200 nm. The shells are expected to act as an electron conduction channel to bring out the inherently high theoretical capacity of phosphorus.

The electrochemical behaviors of the Ni-coated phosphorus composites as a negative electrode for Na-ion batteries are presented in Figure 5a. The specific capacity was calculated on the basis of the weight of an entire active material, including a shell layer. For the 5 wt % Ni coating, the electrode showed an initial discharge capacity of 1760 mA h g⁻¹ with a Coulombic efficiency of 74%. The initial efficiency is equal to that of the black phosphorus electrode, and the overvoltage at 0.63–0.42 V observed only in the black phosphorus electrode was suppressed, which indicates that the α-Ni shell layer functions as an electron conduction channel but not as an inactivator of Na-insertion into phosphorus. We can distinguish four main electrochemical reactions in the differential capacity versus voltage (dQ/dV) curves for all electrodes (Figure 5b). In each electrode, the broad peak that appears between 0.25 and 0.70 V is due to the formation of a surface layer caused by the reduction of an electrolyte and FEC additive and is thereby responsible for the irreversible capacity. A peak observed at 0.65 V is probably associated with the primary sodiation involved in the intercalation of the Na ion into interlayers consisting of phosphorene. Han et al. studied the atomistic sodiation mechanism of black phosphorus using the first-principles calculation. They found that the P–P bond in phosphorus does not break at Na concentrations below Na0.25P, in which only the intercalation reaction occurs. The formation of Na0.33P delivers a capacity of ~220 mA h g⁻¹, and that achieved at approximately 0.65 V is comparable. Sharp peaks at 0.41 and 0.20 V and voltage plateaus shown in the regions between 0.42–0.22 and 0.22–0.18 V are considered to be due to the formation of NaP and Na3P, respectively. For the 30 wt % Ni-coated phosphorus, the electrode exhibited a discharge capacity of 1230 mA h g⁻¹, which is more than quadruple the reversible capacity obtained from carbon-based electrodes, whereas the peak in the dQ/dV profile slightly shifted to the low voltage side. This is because Na-inactive Ni was precipitated on the phosphorus surface even though it is amorphous and relatively thin. There is no remarkable difference on the discharge (Na-extraction) side (Figure S7, Supporting Information).

Figure 6 shows the ex situ XRD patterns of 5 and 30 wt % Ni-coated phosphorus electrodes in the fully sodiated state of 0.005 V and desodiated at 1.5 V under the galvanostatic intermittent titration technique (GITT) condition. At the cutoff voltage of 0.005 V, obvious XRD peaks were observed, which can be attributed to Na13P with a hexagonal structure (P63/mmc (194)/ICSD: 01-073-3917). On the other hand, the peak derived from black phosphorus disappeared at 1.5 V during the discharge state. Sodiation beyond a Na concentration of Na0.28P with a large volume change leads to P intercalation. In addition to phosphorus, the Ni–P alloy detected before the peak evolved into phosphorus at 1.5 V during the desodiation state. Sodiation beyond a Na concentration of Na0.28P with a large volume change leads to P bond cleavage. Silicon (Si) as the negative electrode for LIBs can absorb 3.75 Li by itself to show a high theoretical capacity of 3580 mA h g⁻¹; however, in this case, Si is forced to undergo amorphization by breaking Si–Si bonds induced by the alloying reactions with Li. For the phosphorus-based electrodes, the same explanation as for the Si electrode would apply, which is responsible for the disappearance of the black phosphorus peak. In addition to phosphorus, the Ni–P alloy detected before the charge also disappeared at the desodiated state of 1.5 V. Possible reasons are as follows: (i) formation of nanostructured elemental Ni and P by its phase separation and (ii) crystallinity deterioration or amorphous transformation. However, as much as 30 wt % Ni is contained within the active material. Ni should be detected as a single body if the
phase separation progresses because as much as 30 wt % Ni is incorporated. We therefore consider that the Ni−P alloy undergoes amorphization rather than the phase separation during the sodiation reaction. Even if it is separated, it is expected to be a composite material in which the conductive fine particles are dispersed within the active material. Elucidating the crystallinity and involvement of the shell layer in electrochemical reactions will be studied in the future. Nonetheless, the phase transformation from phosphorus to trisodium phosphide (Na₃P) via three-electron reaction was demonstrated.

Cycling tests were conducted to reveal the influence of the shell layer on the electrode performance for phosphorus-based electrodes (Figure 7). The as-prepared phosphorus resulted in a poor electrode performance. Although a discharge capacity of 1770 mA h g⁻¹ was achieved at the first cycle, the capacity gradually decreased and then rapid-fading suddenly occurred at the 20th cycle, which indicates the electrical isolation of the active material from the current collector. The temporary decline of the Coulombic efficiency around the 23rd cycle is due to the reconstruction of a surface layer through the reductive decomposition of the electrolyte in spite of the use of an FEC additive. A volume expansion/contraction close to 400% occurs in the electrochemical reactions between phosphorus and trisodium phosphide (Na₃P) and thereby pulverizes the active material, followed by the breakup of the surface layer. These are the main reasons for the unfavorable events. It is noteworthy that the capacity fading was effectively suppressed with an increase in the Ni concentration of the shell layer. Although the initial capacity appears to be small as the layer becomes thicker, there is no noticeable difference between the layers based on the capacity per phosphorus, excluding Ni. The 5 wt % Ni-coated composite achieved a higher initial discharge capacity per phosphorus than that of the as-prepared phosphorus, indicating that smooth electron transport occurs inside the active material layer. After the 60th cycle, however, only a capacity of 170 mA h g⁻¹ remained. By contrast, the 30 wt % Ni-coated composite achieved the best electrode performance; a capacity of 780 mA h g⁻¹ was maintained even after the 60th cycle (Figures S8 and S9, Supporting Information). On the other hand, when the capacities are calculated over the entire electrode (30 wt % Ni-coated phosphorus), including conductive additive, binder, and Ni, the discharge capacities at the first and the 60th cycles are 620 and 300 mA h g⁻¹, respectively. Although the relatively good capacity retention was obtained by coating Ni with 30 wt %, the large Ni loading is one of the reasons for the decrease in the effective capacity in batteries. While imparting conductivity with less Ni amount, the achievement of high cycling performance by improvement using other components such as binders and electrolytes is a future study.

We investigated the reaction resistances of the elemental steps during the electrochemical sodiation by EIS measurements using an [electrode|electrolyte|electrode] symmetric cell with two identical negative electrodes charged (Na-inserted) at a rate of 260 mA g⁻¹ (0.1 C). The reversible capacity was calculated based on the weight of the active material including Ni.
on the electrochemical Na-insertion reactions. In the first cycle, the Nyquist plots show two obvious semicircles and a straight line with a slope of approximately 45°. The first semicircle observed in the high-frequency region denotes interfacial Na-ion conduction through an FEC-derived surface layer (interfacial resistance: $R_{\text{fi}}$). The FEC additive electrochemically decomposes before the EC and DEC solvents to form a protective layer that suppresses further electrolyte decomposition. Each size of semicircles corresponding to resistance values is same degree ($\sim$5 Ω), which supports the effect of FEC addition. The second semicircle in the middle frequency region is interpreted as the charge transfer resistance ($R_{\text{ct}}$) involved in the sodiation reaction.  

The as-prepared black phosphorus caused a large charge transfer resistance (25 Ω), which is responsible for the original low electrical conductivity. On the other hand, the resistance values for the 5 and 30 wt % Ni-coated composites became less than half of that for the as-prepared black phosphorus. For the 5 wt % Ni coating, the thickness of the shell layer surrounding the phosphorus is only about 2 nm, whereas the 30 wt % Ni-coated composite has approximately a 200 nm thick layer with Ni inside the core structure in the form of a solid solution. The developed electrical conduction network probably allows for a smooth charge transfer. This is the reason why the Ni-coated composite exhibited a much smaller reaction resistance. After the 30th cycle, no increase in the charge resistance was recognized in the 30 wt % Ni-coated phosphorus (Figure S10, Supporting Information), suggesting the high structural stability of the shell layer as the electrical conduction channel. The favorable effect is reflected in the changes in the electrode thickness after the 30th desodiation, as shown in the cross-sectional FE-SEM images (Figure 9); the electrode is dense compared to the other electrodes, although the electrode thickness before cycling is at the same level. In the black phosphorus electrode, cracks and great porosities were locally generated. The cause of the significant deformation is the inhomogeneous electrochemical reactions. Reversibility of desodiation reactions for the respective active materials is revealed from the surface FE-SEM images of the cycled phosphorus-based electrodes; in the black phosphorus electrode, phosphorus remained expanded after cycling, which indicates that desodiation from non-conductive Na$_3$P formed during the charge reactions did not proceed completely. By contrast, for the Ni-coated composite, irreversible electrochemical reactions were effectively suppressed with an increase in the Ni content (Figure S11, Supporting Information). In the FE-SEM observation and EDS mapping analysis for 30 wt % Ni-coated phosphorus powder peeled off from the electrodes after the first cycle, we can confirm that the mapping image of Ni K$\alpha$ overlaps with that of P K$\alpha$, which indicates the structural integrity of the coating layer on the phosphorus particle. Even after the 10th cycle, Ni element was detected, although the intensity of the X-ray fluorescence was slightly decreased (Figure S12, Supporting Information). The obtained results make it clear that the Ni-based coating layer was held on the phosphorus particle even after charge–discharge processes were involved in volume changes, and that the core–shell structure has high durability. As for the black phosphorus electrode, the active material layer is detached from the current collector, which leads to rapid capacity fading (Figure S13, Supporting Information). Porosities were still confirmed in the 5 wt % Ni-coated phosphorus electrode; however, the degree of porosity is decreased compared with that of black phosphorus. Furthermore, such a change in the electrode structure was suppressed in the 30 wt % Ni-coated composite. It was demonstrated that the Ni/Ni$_3$P shell layer with a conducting pathway also acts as a buffer against the stress induced by the large volumetric change in phosphorus during the sodiation and desodiation reactions. Finally, the rapid discharge property was evaluated at various current densities (Figure 10). With respect to the black...
phosphorus electrode, the capacities were substantially decreased with increasing current density, and only a capacity of 370 mA g\(^{-1}\) remained at 5.0 C. By contrast, the composite electrode showed improved rate capabilities. In particular, 30 wt % Ni-coated phosphorus exhibited a remarkably high performance; a capacity of 940 mA g\(^{-1}\) with a capacity retention of 80% was attained even at a high rate of 5.0 C. Considering the capacity per phosphorus (1340 mA g\(^{P}\)\(^{-1}\)), the value corresponds to 52% of the theoretical capacity of black phosphorus. What these examples make clear is that the conductive pathway inside the electrode to bring out a conductive network granted by the Ni/Ni\(_{3}\)P, NiPH, and NiP\(_{3}\) corresponds to 52% of the theoretical capacity of black phosphorus. Furthermore, the layer granted by the shell layer also activates the reversible Na\(_{+}\) insertion/extraction properties, one of the factors is that the good conducting pathway enhances the utilization of active materials. As a matter of course, one of the factors is that the good conducting pathway granted by the Ni/Ni\(_{3}\)P layer more efficiently transfers the electric charge from the surface toward the center. In addition, metallic Ni formed at the outermost surface. The 30 wt % Ni-coated phosphorus composite exhibited a superior cycling performance to that of the other electrodes; a capacity of 940 mA h g\(^{P}\)\(^{-1}\) was achieved even at a high rate of 5.0 C. Metal coating by electroless deposition at a single particle level should be a powerful yet simple process to improve the reversibility of the electrochemical reactions and the cycling performance of phosphorus-based electrodes.

**CONCLUSIONS**

For achieving high energy density Na-ion batteries, Ni-coated phosphorus was prepared by an electroless deposition technique using milled black phosphorus. The XRD results revealed that Ni was deposited as an amorphous layer on the surface with 10 wt % Ni content. Coating with 20 wt % Ni or more produced a shell with a thickness of ~200 nm in the order of Ni\(_{12}\)P\(_{5}\), NiP\(_{2}\), and NiP\(_{3}\) from the surface toward the center. In addition, metallic Ni formed at the outermost surface. The 30 wt % Ni-coated phosphorus composite exhibited a superior cycling performance to that of the other electrodes; a reversible capacity of 780 mA h g\(^{P}\)\(^{-1}\) corresponding to twice or more of that of the hard carbon electrodes was maintained, even after the 60th cycle. The EIS analysis and cross-sectional FE-SEM observation demonstrated that the Ni/Ni\(_{3}\)P shell played a key role in buffering the large volumetric change in phosphorus during sodium/desodiation rather than in the enhancement of utilization of active materials. As a matter of course, one of the factors is that the good conducting pathway granted by the Ni/Ni\(_{3}\)P shell layer also activates the reversible Na storage reaction of nonconductive NaP. Furthermore, the layer on phosphorus allowed the smooth charge transfer to upgrade the rapid charge—discharge property; a desodiation capacity of 1340 mA g\(^{P}\)\(^{-1}\) was achieved even at a high rate of 5.0 C. Metal coating by electroless deposition at a single particle level should be a powerful yet simple process to improve the reversibility of the electrochemical reactions and the cycling performance of phosphorus-based electrodes.

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