

## Study on manufacture and performance of negative electrode material for Electric vehicle battery

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**Abstract:** In this paper, Ni-NiO/PCNs anode materials were prepared by in-situ synthesis. The effects of sodium chloride template, annealing temperature and annealing time on the phase composition, microstructure and electrochemical properties of the anode materials were compared and analyzed. The results show that Ni/PCNs, Ni-NiO/C and Ni-NiO/PCNs anode materials mainly contain nickel and amorphous carbon phase, and the latter two anode materials also contain nickel oxide phase. 300C / 4h is the suitable annealing process for Ni-NiO/PCNs anode materials, when the Ni-NiO particles in Ni-NiO/PCNs anode materials are well dispersed and maintain three-dimensional lamellar structure, and the average size is about 27nm. If the annealing time is too long (6h), the nickel particles will peroxidize and agglomerate, while too high temperature (400 °C) will make the particles mainly agglomerate and the three-dimensional lamellar structure will disappear. When the current density is 1A/g and the discharge capacity of Ni-NiO/PCNs anode material is 235mA h / g after 5000 cycles, the discharge capacity is about 83.93% of the discharge capacity of the first ring. The discharge capacity and capacity retention of Ni-NiO/C and Ni/PCNs anode materials during charge-discharge cycle and after 5000 cycles are significantly lower than those of Ni-NiO/PCNs anode materials. Ni-NiO/PCNs anode materials have relatively better cycle stability, which is mainly related to their unique porous three-dimensional lamellar structure.

### 1. Introduction

Lithium-ion battery and sodium-ion battery have the same storage mechanism, and compared with lithium-ion battery, sodium-ion battery has the advantages of low cost and abundant sodium source. However, because the radius of sodium ion (0.102nm) of the latter is much larger than that of lithium ion (0.076nm), finding the host material that can stably insert / remove sodium ion in practical application has become the key to the application of sodium-ion battery in new energy vehicles [1].

Although metal oxides with high theoretical capacity (cobalt oxide, iron oxide, nickel oxide, etc.) show good application potential in sodium ion anode materials, however, due to the large volume expansion and low conductivity in the sodium process, the cycle life of sodium ion battery is poor [2].

Nanostructured metal oxides and their composites (MnO<sub>2</sub> nanocrystals, NiO/Ni/ graphene, etc.) can effectively improve the cycle stability, but the durability is poor at high current density [3].

Therefore, it is necessary to further develop anode materials for sodium ion batteries with high cycle stability and durability in order to cushion the problems such as volume expansion and decrease of electrical conductivity in the process of natrifcation.

In this paper, Ni-NiO nano-particles embedded in porous carbon nano-lamellar (PCNs) composites with unique porous lamellar structure were prepared by in-situ synthesis method, in order to provide technical support for the development and application of ultra-long cycle life anode materials for sodium ion batteries [4].

## 2. Experimental materials and methods

### 2.1. Sample preparation

According to the mass ratio of nickel nitrate hexahydrate:ethanol:sodium chloride of 1:3:24, dissolve 16.4g of the mixture in 45mL of water, stir well and place it in a Carbolite HTMA6/220 oven. Set the temperature to 78°C, the drying time is 24h, the dried block sample is mechanically ground into powder; the high-temperature pyrolysis is carried out at 725°C/2h in the CWF11-5 atmosphere heat treatment furnace, and the protective gas is high-purity argon (99.96% ), cool to room temperature naturally after the end, and obtain Ni(NO<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>/NaCl(Ni/C/NaCl) powder; the calcined powder sample will continue to be annealed at 300°C/4h under air atmosphere (Ni-NiO/C/NaCl powder), then washed with deionized water and dried to obtain Ni-NiO/PCNs composite material. For comparison and analysis, Ni-Ni/C and Ni/PCNs composites were prepared without adding NaCl template and without annealing, and the annealing system was optimized (200°C/4h, 300°C/2h, 300°C/6h, 400°C/4h).

### 2.2. Testing and characterization

JEOL6800 scanning electron microscope and JEOL2100 transmission electron microscope were used to observe the microscopic morphology and microstructure of the sample; the phase composition was analyzed by the Paneramic Empyrean X-ray diffractometer, the copper target K $\alpha$  radiation, the scanning angle was 10°~80°; Raman spectroscopy was performed on the sample with RFS100 Raman spectrometer; the pore size distribution of the sample was tested with ASAP2020PLUS specific surface and porosity analyzer; ESCALAB250Xi X-ray photoelectron spectrometer was used Perform XPS spectrum test. The prepared active material, super-p conductive material and binder are mixed uniformly according to the mass ratio of 8:1:1, and then coated on the copper foil, vacuum dried (100°C/15h), punched to make a  $\Phi$ 12mm electrode sheet ; Using the tested electrode sample, sodium foil as the working electrode and counter electrode, glass fiber as the diaphragm, 1:1 mass ratio of ethylene carbonate and dimethyl carbonate as the electrolyte, the button battery is assembled in the glove box. Carry out cyclic voltammetry test (0.01~3V) and electrochemical impedance test (frequency range 100kHz~10MHz) in SeriesG300 electrochemical workstation; Carry out constant current charge and discharge test (0.01~3V) in ITS5300 battery charge and discharge test system.

## 3. Experimental results and analysis

Figure 1 shows the microscopic morphology and structure characterization results of the anode materials Ni/PCNs and Ni-NiO/PCNs for sodium ion batteries. It can be seen from the XRD pattern that there is no NaCl diffraction peak in the XRD patterns of Ni/PCNs and Ni-NiO/PCNs, indicating that deionized water can effectively remove the NaCl template; the former mainly contains Ni and amorphous C phase, the latter It mainly contains Ni, NiO and amorphous C phase (Figure 1a), which indicates that Ni particles will be partially oxidized to NiO during annealing at 300°C/4h. From the scanning electron microscope microscopic morphology, it can be seen that both Ni/PCNs and Ni-NiO/PCNs show a three-dimensional porous connection morphology (Figure 1b, c). It can be seen that Ni particles are embedded in the carbon nanosheets, indicating that the annealing treatment will not the three-dimensional structure of the negative electrode material changes. It can be seen from the Raman spectrum (Figure 1d) that the Ni-NiO/PCNs anode material has a D band at 1342cm<sup>-1</sup> and a G band at 1608cm<sup>-1</sup>. The intensity ratio of the two is about 1.41, which further shows at this time, the carbon nanosheet layer is amorphous C, which is more conducive to the storage of sodium ions in the battery anode material than graphite [8]. It can be seen from the isotherm curve and pore size distribution graph (Figure 1e) that the adsorption and desorption curve of Ni-NiO/PCNs anode material has the characteristics of type IV hysteresis curve, which is mainly related to the large number of mesopores [9], and the pore size distribution Wider and mainly concentrated near 4nm, this porous structure will be more conducive to the transport of electrolyte

and provide more effective active sites for sodium ions. It can be seen from the XPS spectrum (Figure 1f) that the characteristic peaks of the Ni-NiO/PCNs anode material are relatively obvious, C1s is located at 284eV, O1s is located at 533eV, while the characteristic peak of Ni2p is not obvious, which is mainly compared with Ni-NiO particles. Good packaging is related to the three-dimensional sheet structure. This packaging structure can inhibit nanoparticle agglomeration to a certain extent and enhance cycle stability.

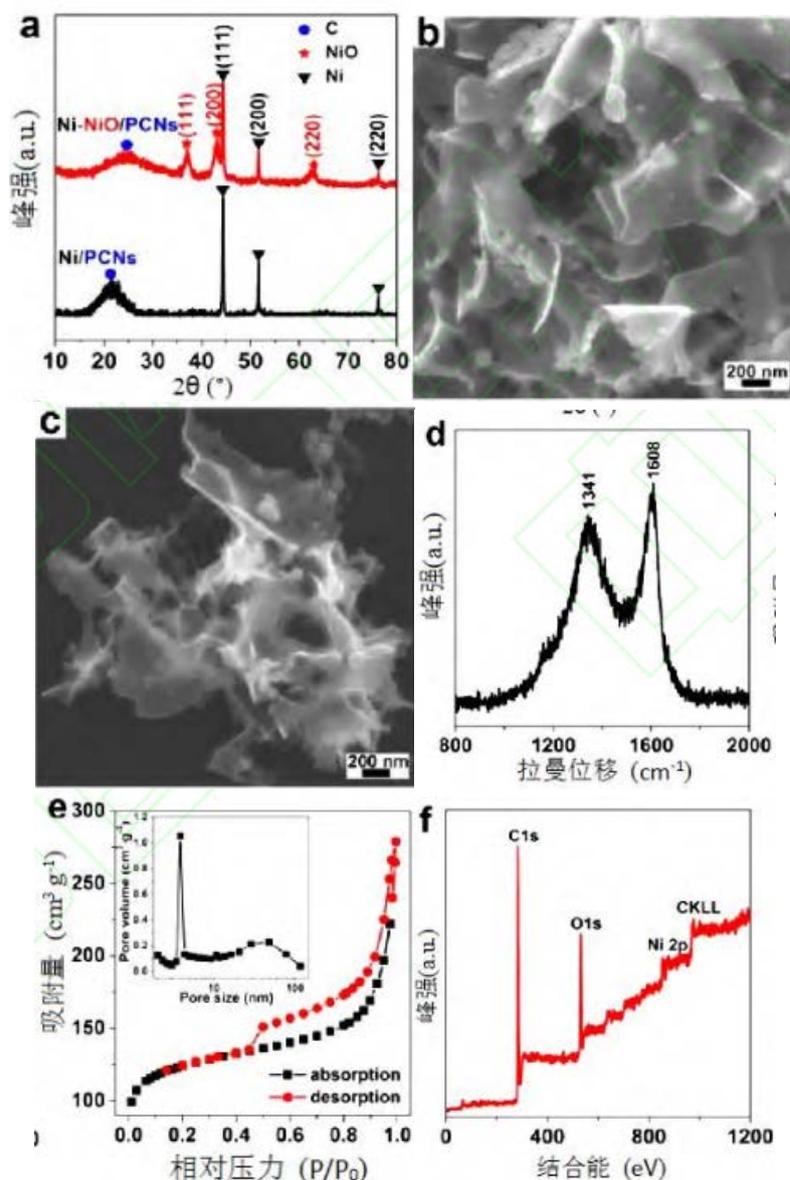


Figure 1 Characterization of Micromorphology and Structure of Anode Materials for Sodium Ion Batteries (a—XRD pattern; b—Ni/PCNs micro morphology; c—Ni-NiO/PCNs micro morphology; d—Ni-NiO/PCNs Raman spectrum; e—Ni-NiO/PCNs isotherm and pore size Distribution; XPS spectrum of f-Ni-NiO/PCNs)

Figure 2 shows the microscopic morphology and structure characterization of the Ni-NiO/C anode material. The annealing process is 300°C/4h. It can be seen that the phases of the Ni-NiO/C negative electrode material without NaCl as the template are similar to Ni-NiO/PCNs, mainly Ni, NiO phase and amorphous C (Figure 2a); the microscopic morphology of Figure 2b can be seen The Ni-NiO/C anode material that does not use NaCl as a template does not exhibit a carbon nanosheet structure, which shows that NaCl is very important for the formation of nanosheets. This is mainly because NaCl can provide a rich surface and promote carbon nanosheets. The formation of the structure; as can be seen from the isotherm curve and pore size distribution diagram (Figure 2c), the

adsorption and desorption curve of Ni-NiO/C anode material also has the characteristics of type IV hysteresis curve, but its pore size is relatively Ni-NiO/. The PCNs anode material is larger, and accordingly the specific surface area will be smaller than the latter.

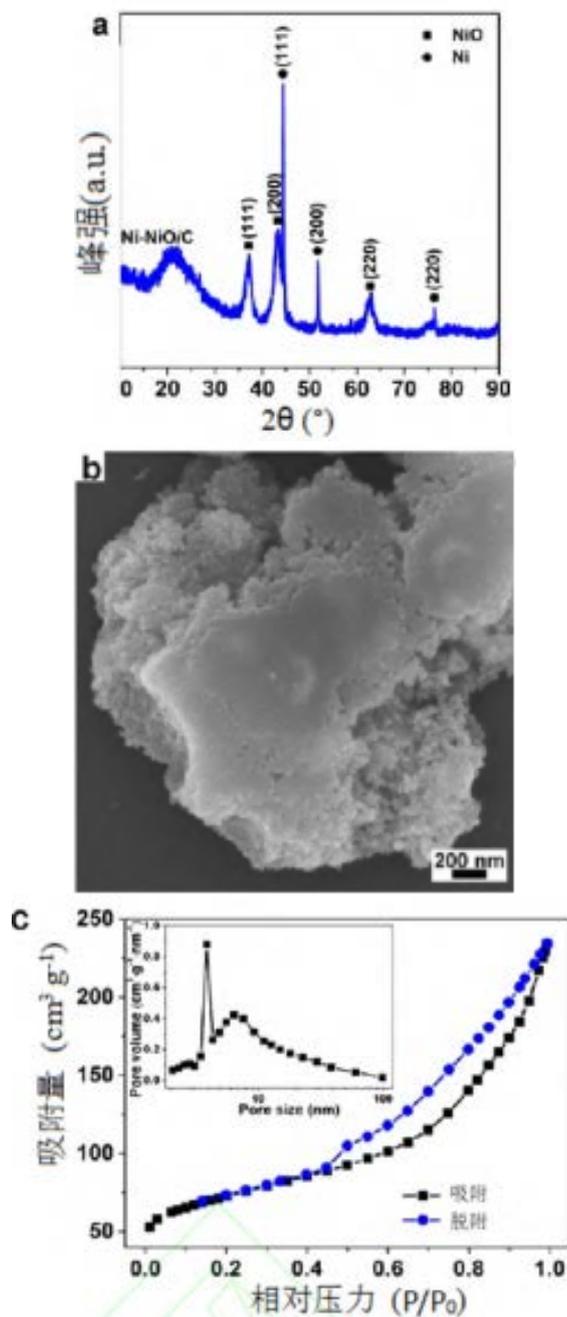


Figure 2 Characterization of Micromorphology and Structure of Ni-NiO/C Anode Materials

Figure 3 shows the microscopic morphology and structure characterization results of Ni-NiO/PCNs anode materials at different annealing temperatures. The annealing time is 4h. It can be seen from the XRD pattern that the phase composition of the Ni-NiO/PCNs anode material after annealing at a lower temperature (200°C/4h) is similar to that during annealing at 300°C/4h, while annealing at a higher temperature (400°C/4h), The Ni-NiO/PCNs anode material mainly contains NiO phase, and the diffraction peaks of Ni phase and amorphous C phase basically disappear, indicating that all Ni particles have been oxidized to NiO during annealing at 400°C. From the microscopic morphology, the sample annealed at 200°C/4h still has the characteristics of lamellar structure, and small Ni nanoparticles can be seen, while the sample annealed at 400°C/4h is mainly particle agglomeration, and the three-dimensional lamellar structure disappears.

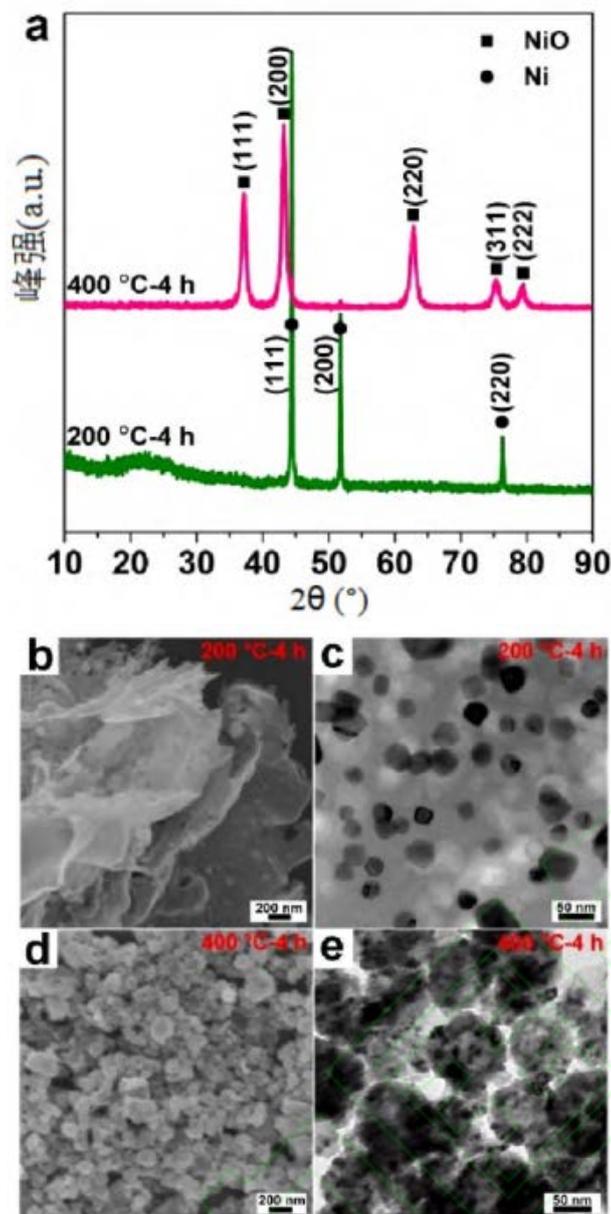


Figure 3 Characterization of Micromorphology and Structure of Ni-NiO/PCNs Anode Materials at Different Annealing Temperatures

Figure 4 shows the microscopic morphology and structure characterization results of Ni-NiO/PCNs anode materials under different annealing times, and the annealing temperature is 300°C. It can be seen from the XRD pattern that the annealing time does not affect the phase composition of the Ni-NiO/PCNs anode material, and the phase under the shorter time (2h) and the longer time (6h) is similar to that of the annealing at 300°C/4h, Are mainly composed of Ni, NiO phase and amorphous C phase. From the microscopic morphology point of view, the Ni particles in the sample with an annealing time of 2h only partially oxidized, and the microscopic morphology still presents a three-dimensional lamellar structure. After a long time, annealing (6h), the Ni particles are oxidized More serious, particle agglomeration can be seen locally. Combined with the observation results in Figure 1, it can be seen that the annealing time will have a significant impact on the microscopic morphology of the Ni-NiO/PCNs anode material. When the annealing time is 4h, the Ni-NiO/PCNs anode material has better dispersibility and maintains A three-dimensional lamella structure.

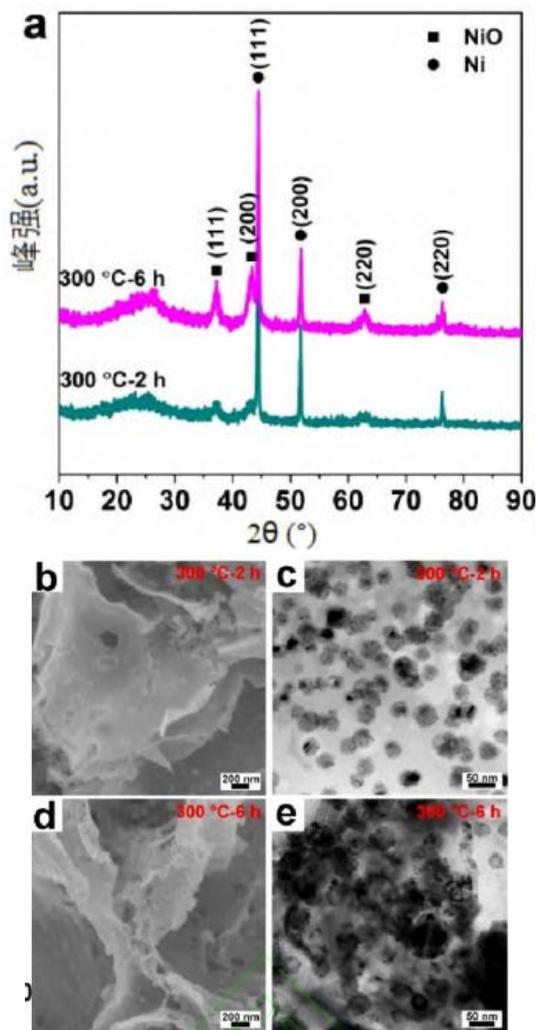


Figure 4 Characterization of the micromorphology and structure of Ni-NiO/PCNs anode materials under different annealing times

Figure 5 shows the observation results of Ni/PCNs and Ni-NiO/PCNs anode materials by high-resolution transmission electron microscopy. It can be seen that the Ni nanoparticles in the Ni/PCNs negative electrode material are characterized by a dispersion distribution, the size is mainly between 20~26nm, and the average size is about 23nm (Figure 5a). The crystal plane spacing of the Ni nanoparticles in the high-resolution transmission electron microscope is 0.203. nm (Figure 5b). The Ni-NiO nanoparticles in the Ni-NiO/PCNs negative electrode material also show the characteristics of dispersion distribution, the size is mainly between 24~30nm, and there are fewer particles with a size less than 24nm, and the average size is about 27nm (Figure 5c). The average size is higher than that of Ni/PCNs; the nanoparticles at this time can be seen in the high-resolution transmission electron microscope composed of Ni particles and NiO particles. Among them, the interplanar spacing of Ni nanoparticles is 0.203nm, and the interplanar spacing of NiO particles is relatively Larger (0.209nm and 0.241nm), and at the same time it can be seen that the Ni-NiO interface presents a semi-coherent feature (box), Ni-NiO has achieved the package of amorphous C. On the whole, the annealed Ni-NiO/PCNs negative electrode material has formed a porous structure due to the Kirkendall effect , that is, due to the diffusion of Ni particles during the annealing process, a vacancy flow is formed and finally aggregated into size The pores are about 4nm, so the reaction will increase the size of Ni-NiO nanoparticles to a certain extent, and this porous structure helps the transport of electrolyte during the charge and discharge cycle and reduces the stress concentration caused by volume changes.

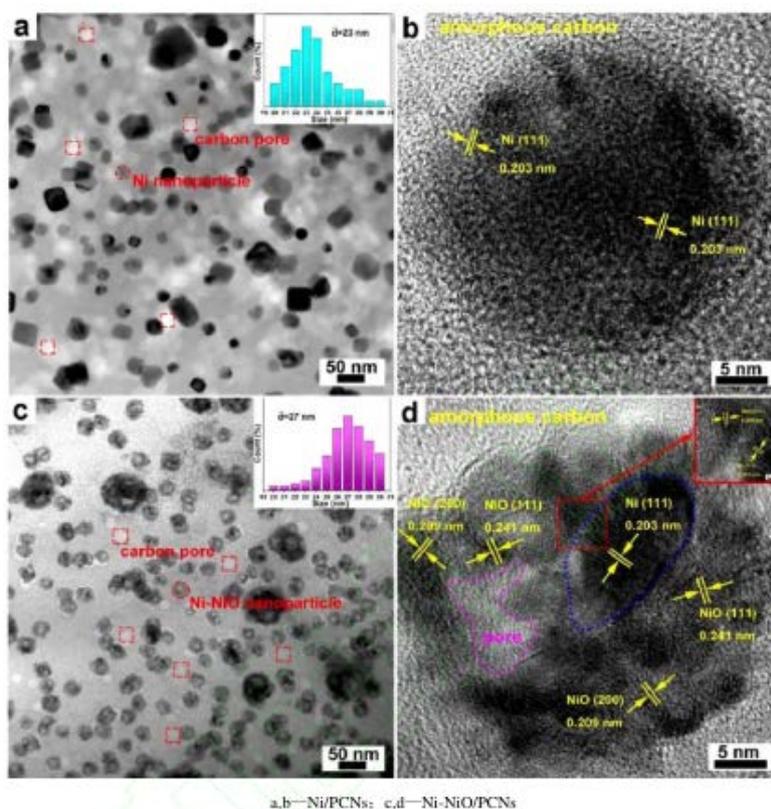


Figure 5 HRTEM morphology of anode material for sodium ion battery

Figure 6 shows the electrochemical performance test results of the negative electrode material Ni-NiO/PCNs for sodium ion batteries. It can be seen from the CV curve that 0.49V corresponds to the formation of an irreversible solid electrolyte interface film in the first circle (1st) discharge curve, 0.9V corresponds to the reduction of NiO, and the voltage corresponding to the cathode peak in the second circle (2nd) discharge curve is positive. The strength is weakened due to the shifting direction, which is mainly related to the relatively stable irreversible solid electrolyte interface membrane; the anode peaks of 1.48V and 0.28V in the charging curve correspond to the oxidation of Ni and a small amount of decomposition of the irreversible solid electrolyte interface membrane, respectively. From the constant current charge-discharge curve (current density 0.1A/g), it can be seen that due to the formation of the irreversible solid electrolyte interface film, the first-lap coulombic efficiency is about 61%, but the initial charge capacity of Ni-NiO/PCNs is still higher than that of NiO the initial discharge capacity of the former is about 1.03 times that of the latter. This is mainly due to the larger specific surface area of the former and the partial decomposition of the irreversible solid electrolyte interface membrane during charging. From the cycle performance curve (current density of 0.1A/g), it can be seen that the cycle stability of the Ni-NiO/PCNs anode material is significantly higher than that of the Ni-NiO/C anode material. After 100 cycles, the discharge capacity of the two are different. It is 447mA•h/g and 131mA•h/g, and the Coulomb efficiency is close to 100% due to the effective insertion/extraction of sodium ions in the Ni-NiO/PCNs anode material. It can be seen from the rate performance curve that when the current density is 0.5, 1, 2 and 0.2A/g, the rate performance of the Ni-NiO/PCNs anode material is significantly higher than that of the Ni-NiO/C anode material. This is because the former is due to the good combination of Ni-NiO and PCNs has relatively high conductivity [18]; in addition, the discharge capacity of Ni-NiO/PCNs anode materials is still higher than that of Ni-NiO/C anode material, and the discharge capacity has been improved, which is mainly related to its relatively stable structure.

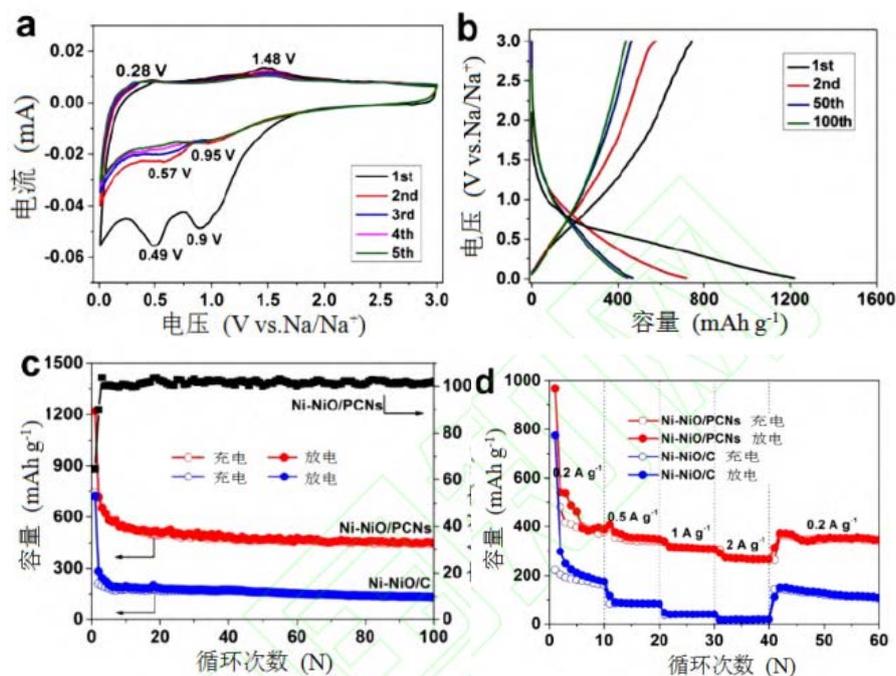


Figure 6 Electrochemical performance of anode materials for sodium ion batteries

#### 4. Conclusion

Ni/PCNs, Ni-NiO/C and Ni-NiO/PCNs anode materials mainly contain Ni and amorphous C phase, and the latter two anode materials also contain NiO phase, which indicates that Ni particles will be affected during annealing at 300°C/4h. Some parts are oxidized to NiO; Ni/PCNs and Ni-NiO/PCNs both present a three-dimensional porous connection morphology. The pore size distribution of the latter is broad and mainly concentrated around 4nm. This porous structure will be more conducive to the transport of electrolyte and it can provide more effective active sites for sodium ions.

300°C/4h is a suitable annealing process for Ni-NiO/PCNs anode materials. At this time, Ni-NiO particles in Ni-NiO/PCNs anode materials have good dispersion and maintain a three-dimensional lamellar structure. The average size is about 27nm. NiO realizes the encapsulation of amorphous C; too long annealing time (6h) will cause Ni particles to over oxidize and agglomerate, while too high temperature (400°C) will cause the particles to be mainly agglomerated and the three-dimensional layered structure disappears.

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