



High-temperature electrochemical performance of Al- α -nickel hydroxides modified by metallic cobalt or Y(OH)₃

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ABSTRACT

Al- α -Ni(OH)₂ microspheres are modified with metallic Co and Y(OH)₃, respectively, in order to improve the high-temperature electrochemical performance. The microstructure, morphology, and surface chemical state of the as-prepared and the modified Al- α -Ni(OH)₂ microspheres are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), respectively. Metallic cobalt nanoparticles are distributed on the nanosheets of the microsphere edges. The existence of metallic Co and Y(OH)₃ can be further verified from ICP and XPS results. The effect of metallic Co or Y(OH)₃ on high-temperature performance of the Al- α -Ni(OH)₂ microspheres is measured by galvanostatic charge–discharge experiments and cyclic voltammetric (CV) measurements. The discharge capacities of the Al- α -Ni(OH)₂ microspheres, with optimized 5 wt% Co and 1 wt% Y(OH)₃, are 283.5 mAh g⁻¹ and 315 mAh g⁻¹, respectively, much higher than that of the as-prepared Al- α -Ni(OH)₂ (226.8 mAh g⁻¹) at 0.2 C and 60 °C. Furthermore, the high-rate discharge capability at high temperature can be also improved for both the modified samples.

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1. Introduction

Nickel-metal hydride (Ni-MH) batteries with high power, high energy density and good safety are promising for hybrid electric vehicles (HEVs), electric vehicles (EVs), electric tools and portable electronic devices. β -Phase nickel hydroxides are widely used as positive electrode materials in commercial Ni-MH batteries. After tremendous efforts over the past decades, the practical discharge capacity of β -phase nickel hydroxides almost reaches to the theoretical capacity (289 mAh g⁻¹) based on one-electron reaction process. α -Phase Ni(OH)₂, with a turbostratic-disordered structure, is one of nickel hydroxide polymorphs [1]. There are more than one electron involved in the electrochemical redox reaction of the α -phase Ni(OH)₂/ γ -phase NiOOH couple. Therefore, α -phase Ni(OH)₂ processes a higher discharge capacity as compared with β -phase Ni(OH)₂ and becomes attractive positive materials for nickel-based alkaline secondary batteries [2–6]. Moreover, α -phase Ni(OH)₂ structure, with high discharge capacity during cycling, can be effectively stabilized by Al substitution [6–12]. Stable Al- α -Ni(OH)₂ microspheres can be subsequently modified with CoOOH nanoparticles to achieve high-rate dis-

charge capability and large discharge capacity in our previous work [13].

In recent years, high-temperature performance of Ni-MH power batteries is of importance for their application in HEVs and EVs, which require to work in an elevated temperature environment over 50 °C. Usually, the high-temperature performance of Ni-MH batteries is mainly determined by nickel hydroxides. Therefore, considerable efforts in the past years were made to improve the high-temperature electrochemical performance of spherical β -Ni(OH)₂. Among all additives, cobalt hydroxides [14,15], calcium hydroxides [16], lanthanide oxides or hydroxides [17–22], and CaF₂/Co(OH)₂, Ca₃(PO₄)₂/Co(OH)₂ or Yb(OH)₃/Co(OH)₂ composites [23–25] were usually added into spherical β -Ni(OH)₂ to improve the high-temperature electrochemical performance. Based on these achievements, the oxygen evolution of spherical β -Ni(OH)₂ by surface modification with metallic cobalt and cobalt hydroxides can be depressed and the charge–discharge reversibility was subsequently improved [15,25,26]. In addition, it was also demonstrated that yttrium compounds were very effective to enhance the charge acceptance of spherical β -Ni(OH)₂ at high-temperature through coating Y(OH)₃ on the surface of nickel hydroxides or adding Y₂O₃ into spherical β -Ni(OH)₂ [19–22]. However, the high-temperature performance of α -Ni(OH)₂ with high discharge capacity is also noticeable for the further practical application [27–29]. It is reasonable that the effective additives used in

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β -Ni(OH)₂ can be selected to improve the high-temperature performance of α -Ni(OH)₂. For example, the discharge capacity of 5.8 mol % Y-doped Al- α -Ni(OH)₂ can reach 250 mAh g⁻¹ at 0.2 C and 60 °C, much higher than that of Al- α -Ni(OH)₂ without Y dopants [29]. In comparison, surface modification with some additives may have a good contribution to the high-temperature performance of α -Ni(OH)₂, because the electrochemical reaction occurs mainly on surface of the active materials.

In this work, Al- α -Ni(OH)₂ microspheres with a high structural stability and a high capacity were synthesized and the high-temperature electrochemical performance was further enhanced by the surface modification with metallic Co or Y(OH)₃.

2. Experimental

2.1. Preparation and characterization

Al-substituted α -nickel hydroxide (Al- α -Ni(OH)₂) was prepared by a homogeneous precipitation method with urea as precipitator [13]. A mixture solution containing Ni(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O ([Ni²⁺] + [Al³⁺] = 0.4 M, [Al³⁺]/{[Ni²⁺] + [Al³⁺]} = 0.1) and 2.0 M urea in a reaction container was heated at 90 °C under a constant magnetic agitating for 12 h. After aging in the mother solution for another 12 h at the same temperature, the green precipitates were separated by filtration, washed several times with de-ionized water to a neutral pH value, washed once with anhydrous ethanol, and dried at 60–65 °C in air.

The procedure of the surface modification with metallic Co: The Al- α -Ni(OH)₂ obtained above was in turn impregnated with PdCl₂ solution (0.4 mol L⁻¹) (in order to activate the surface of the Al- α -Ni(OH)₂ nanosheets), NaH₂PO₂ solution and de-ionized water. The obtained sample was added into a cobalt electroless solution containing cobalt sulfate (25 g L⁻¹), ammonium sulfate (75 g L⁻¹), potassium sodium tartrate (150 g L⁻¹) and NaH₂PO₂ solution (36 g L⁻¹). The mixed solution was maintained under constant magnetic agitating at 75 °C until the color of the solution faded. The pH value was controlled at about 10. The precipitates were filtered, washed with de-ionized water and dried at 60–65 °C. The amount of Co coating was between 3 wt% and 7 wt%, controlled by adjusting the volume of the cobalt electroless solution.

The procedure of the surface modification with Y(OH)₃: The Al- α -Ni(OH)₂ obtained above was dissolved in de-ionized water under constant magnetic agitating at 60 °C. A Y(NO₃)₃ solution (0.02 mol L⁻¹) and NaOH solution (0.06 mol L⁻¹) were dropped stepwise into the above solution at the same time. The suspension was kept in the mother solution for further 12 h at the same temperature. Finally, the solid in the suspension was filtered, washed with de-ionized water several times and dried at 60–65 °C in air. The amount of Y(OH)₃ coating was between 1 wt% and 5 wt%, controlled by adjusting the volume of Y(NO₃)₃ solution and NaOH solution.

All the samples were characterized by X-ray diffraction (XRD, Rigaku D/max-2500) using Cu K α (λ = 1.5406 Å) radiation. The morphology and microstructure were investigated with scanning electron microscope (SEM, Hitachi 3500N) and transmission electron microscope (TEM, FEI Tecnai 20). The surface chemical states of Al- α -Ni(OH)₂ coated with Co or Y(OH)₃ were tested using an X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). Elemental analyses of the metals were conducted on a Thermo Jarrell–Ash model inductively coupled plasma emission spectrometer [ICP, IRIS Advantage].

2.2. Electrochemical measurements

The Al-substituted nickel hydroxide (as-prepared or coated), Ni powders and cobalt oxide powders, were mixed with a weight ratio

of 65.6:26.7:7.7. A 1.0 wt% binder (hydroxypropyl methylcellulose, HPMC) was added to the mixture to obtain a paste, which was incorporated into nickel foam (2.0 cm × 2.0 cm). The obtained nickel electrodes were dried at 50 °C, and then pressed under 30 MPa. The electrodes were subsequently soaked in 6 M KOH for 24 h. Next, the resulting electrode was coupled with a standard AB₅-type hydrogen storage alloy (MmNi_{3.6}Co_{0.75}Mn_{0.35}Al_{0.3}) electrode and an Hg/HgO electrode was used as reference. The cell was charged at 0.1 C for 15 h, discharged at 0.2 C for eight cycles at room temperature. The cut-off potential was 0.1 V (vs. Hg/HgO). Subsequently, high-temperature performance was tested under the following mode: charging at 0.2 C for 7.5 h, and then discharging at 0.2 C, 1 C, 2 C, 5 C and 10 C to 0.1 V at 60 °C, respectively. Cyclic voltammograms (CVs) studies were carried out in a three-electrode model cell at 20 °C and 60 °C, respectively, using a Zahner IM6e electrochemical workstation. The scan rate for CVs was 0.2 mV s⁻¹ in the potential range of 0–0.7 V vs. Hg/HgO electrode.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-prepared Al- α -Ni(OH)₂ and the samples modified with Co or Y(OH)₃. All the diffraction peaks of the as-prepared sample and Al- α -Ni(OH)₂ samples modified with Co or Y(OH)₃ coating can be indexed as a pure α -phase Ni(OH)₂ with a rhombohedral structure. No diffraction peaks of metallic cobalt and Y(OH)₃ or Y₂O₃ can be observed since the coated content of

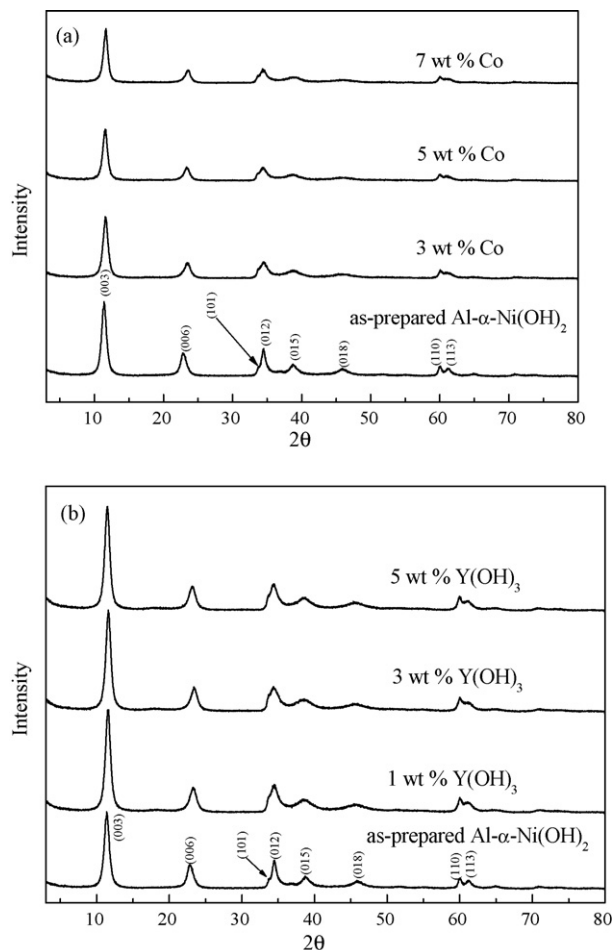


Fig. 1. XRD patterns of Al- α -Ni(OH)₂ microspheres with and without (a) metallic Co and (b) Y(OH)₃.

Co or $Y(OH)_3$ is small. The diffraction intensity of (003) and (006) planes of $\alpha-Ni(OH)_2$ decreases to a certain extent after electroless cobalt plating, as indicated in Fig. 1a, while the intensity increases slightly after coating with $Y(OH)_3$, as shown in Fig. 1b. Moreover, the

asymmetric nature of the reflection near the (101) plane and the broad peaks between 34° and 50° become obvious, indicating the formation of a turbostratic phase [30] during the coating processes with Co and $Y(OH)_3$.

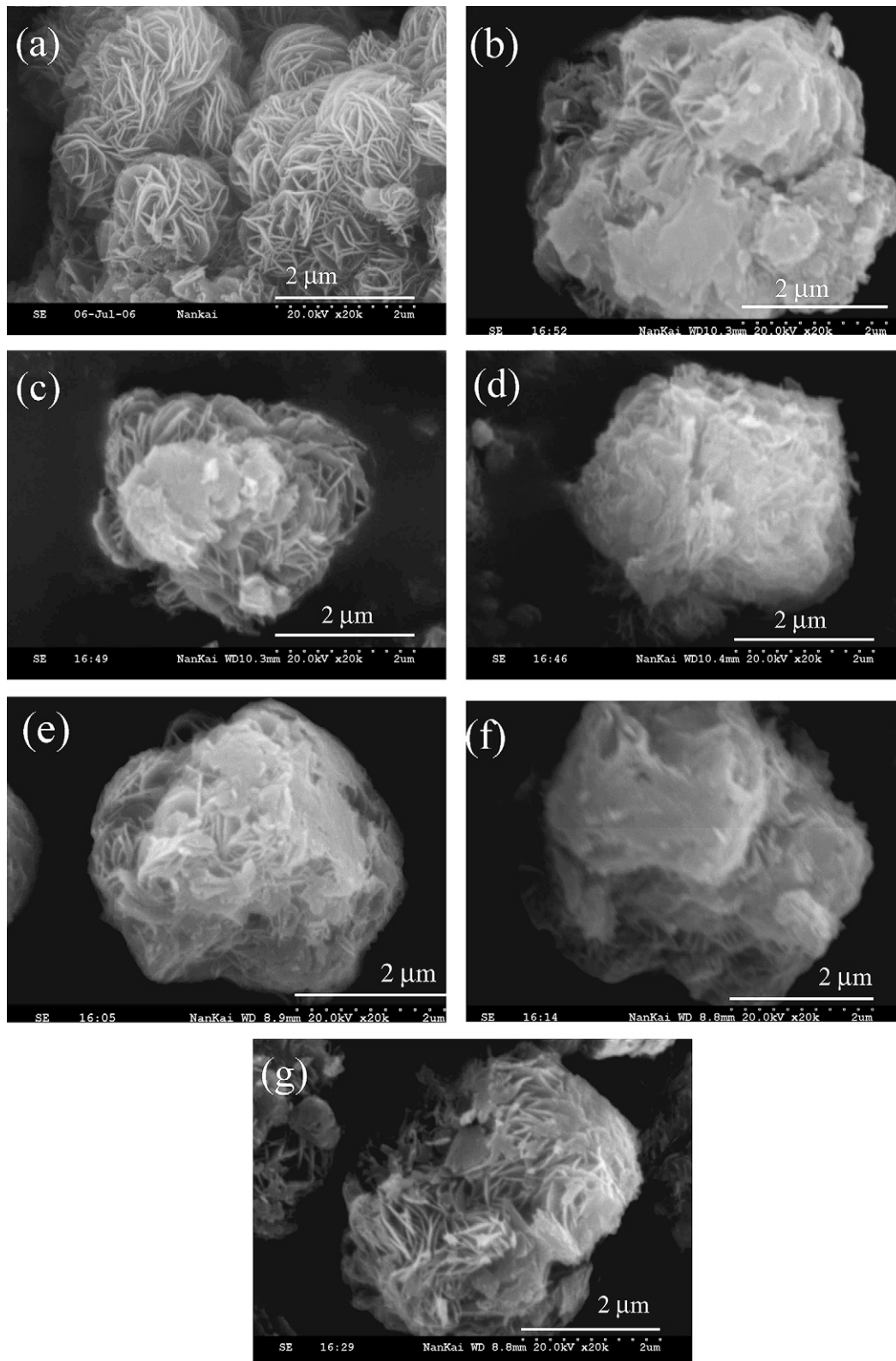


Fig. 2. SEM images of the as-prepared $Al-\alpha-Ni(OH)_2$ (a), and $Al-\alpha-Ni(OH)_2$ microspheres modified with 3 wt% Co (b); 5 wt% Co (c); 7 wt% Co (d), 1 wt% $Y(OH)_3$ (e), 3 wt% $Y(OH)_3$ (f), and 5 wt% $Y(OH)_3$ (g).

SEM images of the as-prepared Al- α -Ni(OH)₂ microspheres and the samples modified with Co or Y(OH)₃ are presented in Fig. 2. The as-prepared sample (Fig. 2a) is sphere-like aggregates of thin plates with clean surface and clear edges, which are 1–2 μ m in diameter. The surface of the nanosheets modified with Co in Fig. 2b–d or Y(OH)₃ in Fig. 2e–g becomes coarse compared with the as-prepared sample, though the sphere-like aggregate morphology still appears. It seems that the second treatment process for coating Co or Y(OH)₃ results in a rough surface of Al- α -Ni(OH)₂ microspheres. It is hard to identify Co or Y(OH)₃ nanoparticles from the SEM images due to the limited resolution, which is similar to the modified Al- α -Ni(OH)₂ with CoOOH nanoparticles [13]. Thus, XPS spectra and TEM images are further conducted to confirm the presence of metallic Co and Y(OH)₃ on the surface of Al- α -Ni(OH)₂ microspheres in the following section.

The relationship between the discharge capacity at 60 °C and the coated amount of Co or Y(OH)₃ nanoparticles on the surface of the Al- α -Ni(OH)₂ microspheres at the discharge rate of 0.2 C, 1.0 C and 2.0 C is shown in Fig. 3. As can be seen in Fig. 3a, the discharge capacity at the elevated temperature increases until the coated amount of Co reaches up to 5 wt%, while further increasing the coated amount up to 7 wt% results in the decrease of the discharge capacity. It is well known that metallic Co is converted to high conductive CoOOH networks during the electrochemical reaction in the charge process, which can improve the surface activities

and depress the oxygen evolution. However, an excess amount of metallic Co leads to the decrease of the discharge capacity due to the lower electrochemical capacity of CoOOH nanoparticles, similar to that of the β -Ni(OH)₂ electrodes with Co or CoOOH [26,31,32]. Al- α -Ni(OH)₂ microspheres modified with Y(OH)₃ have the similar result whereas the optimal amount of Y(OH)₃ is 1 wt%. It is reported that the rare earth oxides can be converted to a thin film of hydrous hydroxides with a worse conductivity on the surface of the spherical β -Ni(OH)₂ in the concentrated alkaline solution, which could inhibit the electron transfer and depress the oxygen evolution [17]. Therefore, the potential of the oxygen evolution is elevated and the charge efficiency of the electrode is also improved, all of which are beneficial for the electrochemical performance at elevated temperature. However, the discharge capacity would decline for the excess rare earth hydroxides in the electrode because of their poor conductivity and lack of the electrochemical capacity. Therefore, when the amount of the Y(OH)₃ on the surface of the Al- α -Ni(OH)₂ exceeds 1 wt%, the discharge capacity at 60 °C decreases contrarily under all the discharge conditions. Thus, the microstructure and electrochemical performance of Al- α -Ni(OH)₂ microspheres modified with 5 wt% Co or 1 wt% Y(OH)₃ are further investigated in detail.

According to the ICP analysis, the metallic Co and Y(OH)₃ amounts of the modified Al- α -Ni(OH)₂ microspheres are 4.7 wt% and 0.78 wt%, respectively, close to their desired values. To further confirm the surface chemical state, the Co2p and Ni2p core level spectra of the Al- α -Ni(OH)₂ with 5 wt% Co are shown in Fig. 4a. The characteristic peak (binding energy) of the Co2p locates at 778.08 eV, in agreement with metallic cobalt state. The nickel exists as Ni(II) oxidation state (853.90 eV) indicating that the reduction is limited only to the formation of metallic Co during the process of electroless cobalt plating. The Y2p, Ni2p core level spectra of the Al- α -Ni(OH)₂ microspheres with 1 wt% Y(OH)₃ are indicated in Fig. 4b. As expected, Ni and Y in the modified Al- α -Ni(OH)₂ microspheres exist as Ni(II) (853.9 eV) and Y(III) (157.9 eV), respectively. However, no reduction or oxidation reactions were accompanied with the surface modification process of Al- α -Ni(OH)₂ microspheres with Y(OH)₃.

TEM images of Al- α -Ni(OH)₂ microspheres with 5 wt% Co are illustrated in Fig. 5. The sample still consists of nanosheets after electroless cobalt plating, which aggregate to form microspheres. Dark areas can be observed clearly from the HRTEM image on the nanosheets of the edges, which are metallic Co nanoparticles according to mass-thickness contrast. It is noted that distinguishing Y(OH)₃ nanoparticles is difficult in TEM observation for Al- α -Ni(OH)₂ microspheres with 1 wt% Y(OH)₃ because of the lower amount of Y(OH)₃ (only 0.78 wt%) from ICP analysis, although Y2p signal on the surface of the sample can be clearly detected in XPS spectra.

Discharge curves at 60 °C of the as-prepared sample and the modified samples with 5 wt% Co and 1 wt% Y(OH)₃ are depicted in Fig. 6. The three samples have a similar single higher discharge potential plateau at 0.2 C, which is a discharge characteristic of α -phase nickel hydroxides [6,10]. However, the high-temperature discharge capacities of the Al- α -Ni(OH)₂ microspheres, with 5 wt% Co or 1 wt% Y(OH)₃, is much higher than that of the as-prepared sample under the same discharge conditions. The discharge capacities at 0.2 C increase up to 283.5 mAh g⁻¹ for the sample modified with 5 wt% Co, and 315 mAh g⁻¹ for the sample modified with 1 wt% Y(OH)₃, while the as-prepared sample has lower capacity of 226.8 mAh g⁻¹. Moreover, the high-temperature discharge capacities of both modified samples at the high-discharge rate are more superior as compared to that of the as-prepared sample. The high-temperature discharge capacities of the as-prepared sample, the sample with 5 wt% Co, and the sample with 1 wt% Y(OH)₃ at 10 C are 164.1 mAh g⁻¹, 197.4 mAh g⁻¹ and 218.4 mAh g⁻¹, respectively.

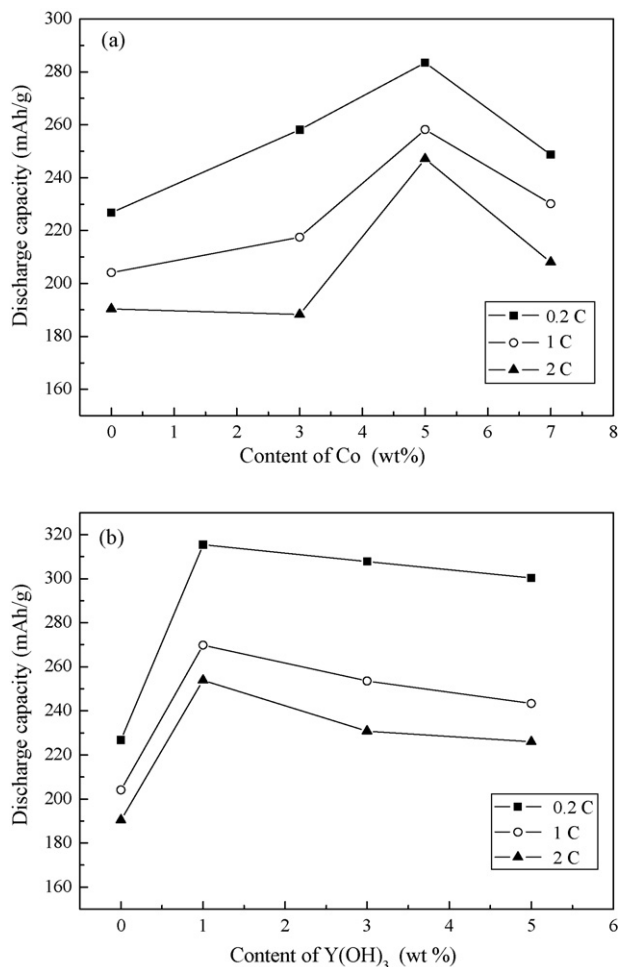


Fig. 3. The variation of the discharge capacity against the amount of Co (a) and Y(OH)₃ (b) for the Al- α -Ni(OH)₂ microspheres at 60 °C. (Discharge rate: 0.2 C, 1 C and 2 C).

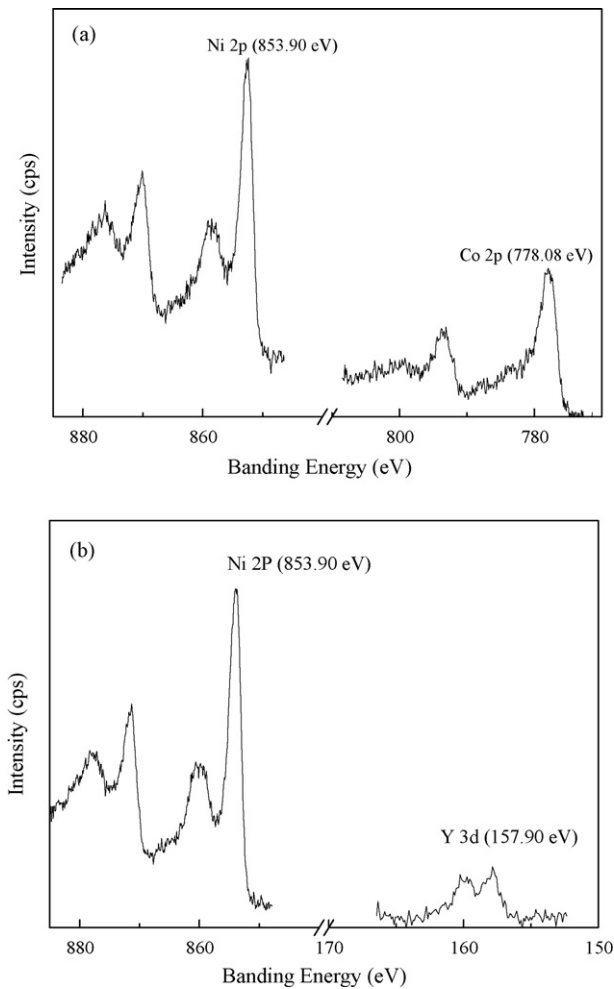


Fig. 4. Co2p, Ni2p and Y3d, Ni2p core level spectra of the Al- α -Ni(OH)₂ microspheres modified with 5 wt% Co (a), and 1 wt% Y(OH)₃ (b), respectively.

The modification with metallic Co and Y(OH)₃ can enhance the discharge capacity and improve the high-rate discharge capability at 60 °C. Relative to metallic Co, Y(OH)₃ is more effective for improving high-temperature electrochemical performance of the Al- α -Ni(OH)₂ microspheres.

To get an insight into the effect of the metallic Co and Y(OH)₃ on the high-temperature performance, the charge curves at 0.2 C and 60 °C of the as-prepared sample, the samples with 5 wt% Co and 1 wt% Y(OH)₃ are presented in Fig. 7. It is clear that there is only one charge flat potential plateau for the as-prepared sample, which means that the charge process and the oxygen evolution process are simultaneous. On the contrary, the second charge plateau potential appears for both the modified Al- α -Ni(OH)₂ microspheres. The oxygen over-potential is defined as the difference between the oxygen evolution potential and the charge plateau potential, and it is

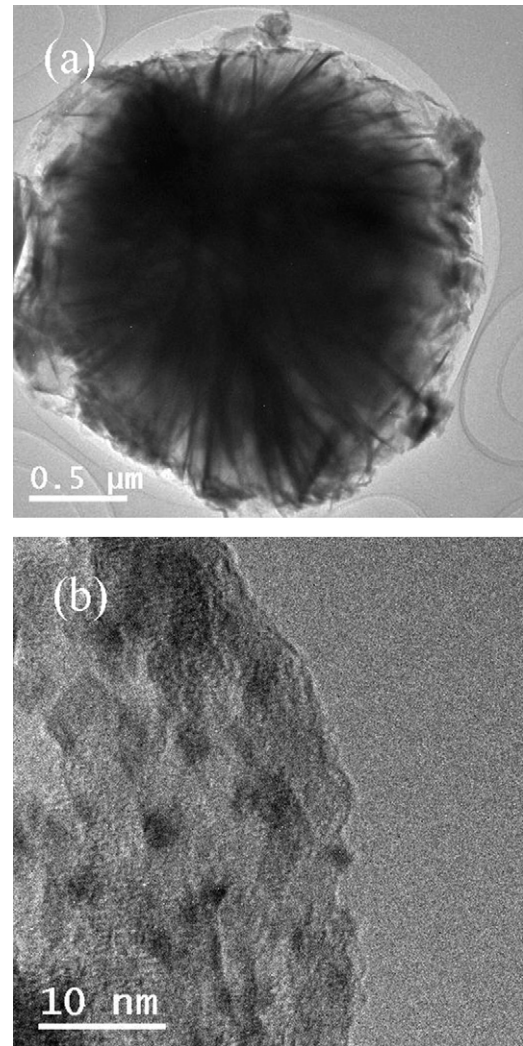


Fig. 5. TEM images of Al- α -Ni(OH)₂ microspheres modified with 5 wt% Co.

the key factor to affect high-temperature performance and electrochemical stability of nickel hydroxides [17,25,32–36]. The larger oxygen over-potential can lead to the higher charge efficiency and charge acceptance [17,37]. Both the samples with 5 wt% Co and 1 wt% Y(OH)₃ have the higher oxygen over-potential, especially the latter one, which leads to the higher discharge capacity at high temperature as shown in Fig. 6.

In order to further confirm the effect of the metallic Co and Y(OH)₃ on high-temperature performance, CVs are carried out at room temperature and 60 °C with the scan rate of 0.2 mV s⁻¹ and illustrated in Fig. 8. The corresponding electrochemical parameters are summarized in Table 1. The difference (oxygen over-potential) between the oxygen evolution potential (E_{oe}) and the oxidation

Table 1
Electrochemical parameters from CVs of the three samples.

Sample	Room temperature			60 °C		
	E_o (mV)	E_{oe} (mV)	$\Delta(E_{oe} - E_o)$ (mV)	E_o (mV)	E_{oe} (mV)	$\Delta(E_{oe} - E_o)$ (mV)
Al- α -Ni(OH) ₂	532	582	50	507	526	19
5 wt% Co Al- α -Ni(OH) ₂	531	600	69	490	540	50
1 wt% Y(OH) ₃ -Al- α -Ni(OH) ₂	507	596	89	470	538	68

E_o and E_{oe} are defined as oxidation potential and oxygen evolution potential, respectively.

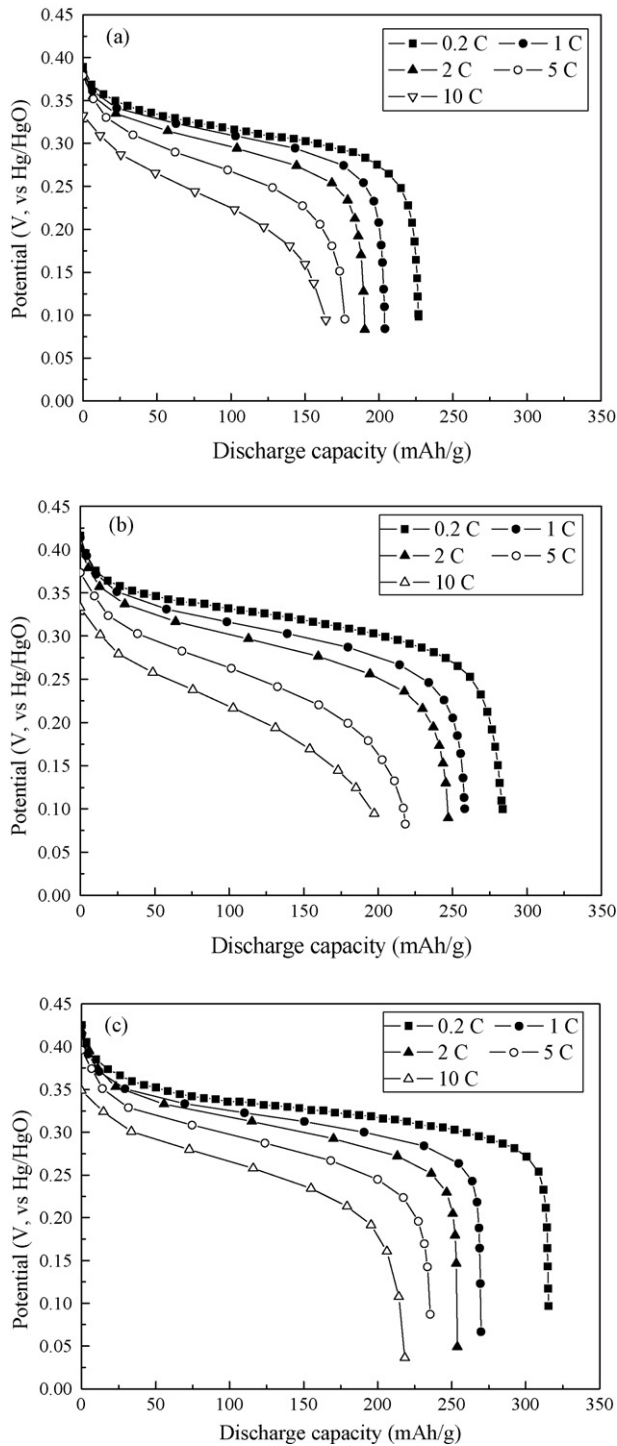


Fig. 6. Discharge curves of the as-prepared Al- α -Ni(OH)₂ microspheres (a), samples modified with 5 wt% Co (b), and with 1 wt% Y(OH)₃ (c) at the different discharge rate.

potential (E_o) is defined as $\Delta(E_{oe} - E_o)$, which is usually used as the indicator of charge efficiency and charge acceptance [23,32,37]. It is found that there is only one anodic (oxidation) and one cathodic (reduction) peak in the curves for the three samples at room temperature and at high temperature (60 °C). The oxygen over-potential ($\Delta(E_{oe} - E_o)$) of the samples with 5 wt% Co and with 1 wt% Y(OH)₃ is much higher than that of the as-prepared sample. Especially at 60 °C, the oxygen over-potential of the as-prepared sample is only 19 mV, indicating that the oxygen evolution reaction is more seri-

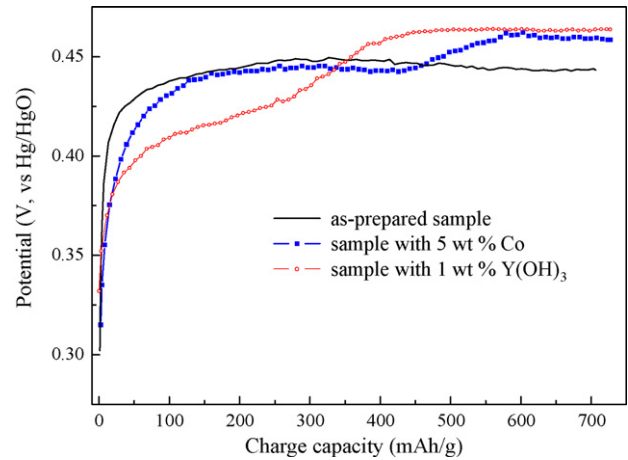


Fig. 7. Charge curves of as-prepared and modified Al- α -Ni(OH)₂ microspheres with 5 wt% Co and with 1 wt% Y(OH)₃ at 0.2 C and 60 °C.

ous. While the oxygen over-potentials for the Al- α -Ni(OH)₂ with 5 wt% Co and 1 wt% Y(OH)₃ are 50 mV and 68 mV, respectively, in good agreement with the above results of the charge curves in Fig. 7. Therefore, both the modified samples have an improved charge acceptance at 60 °C.

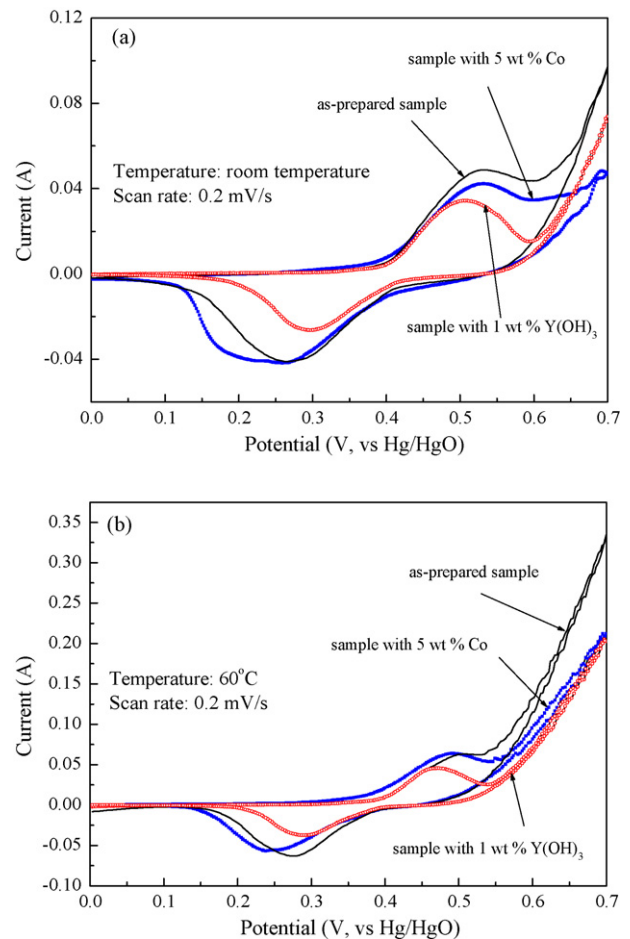


Fig. 8. Cyclic voltammograms of the as-prepared and modified Al- α -Ni(OH)₂ microspheres with 5 wt% Co and with 1 wt% Y(OH)₃ at room temperature (a) and 60 °C (b).

4. Conclusion

Al-substituted α -Ni(OH)₂ microspheres are prepared, and surface modifications with metallic Co and Y(OH)₃ are conducted subsequently. It is found from SEM and TEM images that both the as-prepared and the modified Al- α -Ni(OH)₂ microspheres are sphere-like aggregates of nanosheets. Metallic cobalt nanoparticles are distributed on the nanosheets of the microsphere edges, and Y(OH)₃ nanoparticles are hardly observed directly from TEM images due to the low content of Y(OH)₃. However, the existence of metallic Co and Y(OH)₃ can be verified from ICP and XPS results. It reveals that the Al- α -Ni(OH)₂ microspheres with Co or Y(OH)₃ have good charge acceptance at 60 °C. The discharge capacities of the Al- α -Ni(OH)₂ microspheres with 5 wt% Co and 1 wt% Y(OH)₃ are 283.5 mAh g⁻¹ and 315 mAh g⁻¹, respectively, much higher than that of the as-prepared Al- α -Ni(OH)₂ microspheres (226.8 mAh g⁻¹) at 0.2 C and high temperature (60 °C). The improvement of high-temperature performance for the Al- α -Ni(OH)₂ microspheres is mainly contributed to the inhibition of the oxygen evolution process by the surface modification with metallic Co or Y(OH)₃.

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