Nanoporous Ni-Al alloy by De-alloying for Electrocatalytic hydrogen Evolution Reaction

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Abstract: As the main method to solve the current problem about energy shortage and environment pollution, hydrogen production via overall water splitting exhibits great prospects. The Pt-based metals were acknowledged as the optimal electrocatalysts for hydrogen evolution reaction (HER) but cannot be used commercially due to the exorbitant price. In this work, nano-porous Ni was successfully obtained through one-pot de-alloying with different atomic ratio of Ni-Al precursor (Ni\textsubscript{25}Al\textsubscript{75}, Ni\textsubscript{15}Al\textsubscript{85}, Ni\textsubscript{10}Al\textsubscript{90}). The electrochemistry testing results show that the Ni\textsubscript{10}Al\textsubscript{90} provide a lowest onset overpotential with -1.44V for HER. Besides, the potential decrease non-significantly after 1000 cycles of cyclic voltammetry demonstrates a considerable durability.

1. Introduction
With the continuous progress of society, environmental pollution has increasingly become a major problem affecting people's living standards. Hydrogen, as a clean energy source with high energy density, has been regarded as the solution the best choice to solve the problem of energy crisis and environmental pollution\cite{1-3}. At present, the electrochemical water splitting is a promising hydrogen production technology due to the green process, the high purity of product and the effective application of renewable energy. Water electrolysis is a promising approach to produce hydrogen with high efficiency and environmental amity merits\cite{4}. Owing to the inevitable dynamic overpotential in the hydrogen evolution reaction (HER), it demands highly efficient catalyst to overcome the sluggish kinetics\cite{5}. Noble metal and noble metal-based materials are considered as the most active catalyst for HER, but the large scale application is limited by the high cost and low reserve. Therefore, people turn their attention to Ni, Mo, Co, Fe and other metals or alloys\cite{6-7}.

Recently, many researchers have focused on electrocatalysts based on transition metal Ni. Due to its abundant natural resources and low price, it has been found that hydrogen evolution electrocatalysts based on Ni have good performance, low overpotential and excellent stability\cite{8-9}. In addition, it was
found that electrocatalysts containing nickel could expose more active sites to improve catalytic activity[10].

K.I. Siwek reported that 3D Ni foams are obtained from different composition baths by galvanostatic electrodeposition in the hydrogen evolution regime on stainless steel current collectors, the results suggest that the foams morphology, as well as porosity, plays an important role in the determination of the catalytic efficiency of the material and can be easily controlled by changing the electrodeposition process conditions, namely the electrolytic bath composition[11]. However, electrodeposition is a multistep process with low deposition rate. Paserin.V made the capability of the CVD technique to produce uniform foams of different properties, with cell size ranging from ~450 to ~3200um, porosity from 70–98%, and nominal thickness up to 3mm is presented[12]. Yingfei Ma prepared nickel hydroxide with different nanometer spheres by hydrothermal method with different base sources and anions[13]. They suggested that combining the selections of alkaline source and anion could be helpful for controlling the structures and morphologies of transition metal hydroxides. While transition metal have already shown high performance and promising potential as HER catalysts, there are few reports dedicated to improving the heterostructure of transition metal by dealloying[14].

Dealloying has emerged as a convenient and versatile method for making nanoporous metal with high structural definition[15-16]. Dealloying is the selective dissolution of less noble elements from an alloy, leaving behind a porous structure. The nano-porous materials prepared by dealloying method have large specific surface area, and the unique double-continuous structure of pore wall-channel and varied materials are considered to be ideal electrode and catalyst materials[17-19]. In this study, 3 kinds of Ni100-xAlx precursor alloys with different components were prepared by vacuum melting and rapid solidification, and nano porous Ni was prepared by dealloying. The morphology and structure of nano porous Ni obtained from different alloys were investigated. The nano porous Ni coating was made on the surface of glassy carbon electrode, the np Ni electrodes were prepared and their hydrogen evolution properties were studied by linear scanning voltammetry (LSV) and ac impedance.

2. Experimental section

2.1. Material preparation

In the experiment, the purity of the pure metal block was analyzed as Ni_xAl_{100-x} (at.%) according to the atomic ratio, as shown in table 1. Clean the metal block with acetone and alcohol. The prepared metal blocks were put into copper crucible for melting in the order of high melting point to low melting point in a vacuum suspension melting furnace. Increase the heating power at the speed of 0.2kw /30s, and keep it for 1 minute when it is increased to 7kw. Repeat the above operation twice. Cut the melted alloy ingots into small pieces and remove the surface scale, clean them with a large amount of alcohol, and put the appropriate amount of alloy into a quartz glass tube with a nozzle of 1.8cm in diameter (aperture of 1.0mm) after drying. Put it into a vacuum belt slasher and vacuum it with high purity argon gas to 10-3pa. The speed of the roller is adjusted to 25rpm through the copper roller revolution control device, and the required alloy strip is made by rapid cooling. The alloy strips obtained by rapid solidification were immersed in the 25wt.% KOH solution at 65℃ for 32 hours. The alloy strips after dealloying were successively washed with a large amount of distilled water and alcohol until neutral, and then put into a vacuum drying box and dried at 60℃ for 6 hours.

| Table 1. Chemical composition of Ni-Al alloy |
|------------------|------------------|------------------|
| Ni_xAl_{100-x}(at.%) | Ni/wt.% | Al/wt.% |
| Ni_{25}Al_{75} | 42.03 | 57.97 |
| Ni_{15}Al_{85} | 27.75 | 72.25 |
2.2. Preparation of working electrode
Firstly, the glassy carbon electrode (GCE) was polished with polishing fluid. And then the GCE was washed by Ethanol, acetone, HNO₃(1:3), deionized water, respectively. After thorough cleaning, the glassy carbon electrode was placed in 1mol/L H₂SO₄, and electrochemical activation was performed by cyclic voltammetry. The scanning range was -1.0 ~ 1.0V, and the glassy carbon electrode was repeatedly scanned until stable. Then, the electrode performance was tested in 0.20mol/L KNO₃, 1×10⁻³mol/L K₃Fe(CN)₆ solution, the scanning speed was 50mV/s, the scanning range was -0.1 ~ 0.6V, and the cyclic voltammetric test was carried out. Cleaning the treated glassy carbon electrode with deionized water and baking it under the infrared lamp for 30min.

The nano-porous Ni material grinding into powder, and a turbid liquid was acquired comprised of 10mg active substances and 20mL Nafion solution, 480μL deionized water, 500μL ethanol. The turbid liquid was ultrasonic 20 min. The working electrode was prepared by taking 4μL of mixed liquid drops from the pipette and baking them under the infrared lamp for 10min.

2.3. Material characterizations
The phase of the strip and dealloyed samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2400, Cu-Kα, 40kV). The morphology of the fabricated samples were evaluated by field emission scanning electron microscopy (SEM JSM-6700F) and transmission electron microscopy (TEM, JEM-2010) and high-resolution transmission electron microscopic images (HRTEM). The crystal structure was proven by the selected area electron diffraction (SAED) model. The specific surface area was investigated using a nitrogen adsorption-desorption isotherm acquired on a Micro ASAP 2020 analyzer on the basis of the Brunauer-Emmett-Teller (BET) equation.

2.4. Electrochemical measurements
Electrochemical measurements were performed with the CHI660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. The sample were used as the working electrode. A platinum foil (1cm×1cm) and saturated calomel electrode (SCE 1M NaOH) were used as the counter electrode and the reference electrode, respectively. The system was purged with high-purity nitrogen (N₂, 99.99%) for 30 min before the reaction, and the bubbling was maintained throughout the electrochemical experiment.

3. Results and discussion
3.1. Organizational Analysis
Figure 1(a) shows the X-ray diffraction images of the precursor of the Ni-Al alloy strip with three different components obtained by rapid sling. It can be seen from the figure that Ni₁₀Al₉₀ is composed of single-phase NiAl₃, and both Ni₁₅Al₈₅ and Ni₁₀Al₉₀ are composed of two phases, Al and NiAl₃. Ni-Al alloy strips with three different components were placed in wt(NaOH)=25% solution and dealloyed at 65°C for 32h. It can be found that when the alloy strip is just put into NaOH solution, a large number of bubbles are generated, resulting in a violent reaction and a rapid rise in the temperature of NaOH solution. This is the exothermic reaction between NaOH and Al. The reaction equation is as follows:

\[ Al + 2OH^- = AlO_2^{2-} + H_2 \uparrow \]  

(1)

With the prolongation of the reaction time, the intensity of the reaction decreases until there is no bubble. At this time, the Ni-Al alloy strip is black and has no silver-white metallic luster. Figure 1(b) shows the XRD pattern of the strip of Ni-Al alloy with three different components after dealloying. From the figure, Ni₂₅Al₇₅, Ni₁₅Al₈₅ and Ni₁₀Al₉₀ were dealloyed to obtain a single plane-center cubic Ni, Al phase not observed, indicating that the dealloying was complete.
Figure 1. (a, b) XRD patterns of \( \text{Ni}_{100-x}\text{Al}_x \) alloy before and after dealloying.

Figure 2 shows the SEM appearance morphology of Ni-Al alloy with three different components after 32h dealloying. It can be seen from the SEM figure that the morphology of the dealloyed Ni-Al alloy with different components is obviously different. The Ni skeleton size and small pore size of \( \text{Ni}_{25}\text{Al}_{75} \) were 200~300nm and 100~200nm respectively. \( \text{Ni}_{25}\text{Al}_{75} \) is composed of a single NiAl\(_3\) phase, which is prone to be corroded in NaOH solution. When the NiAl\(_3\) phase reacts with NaOH solution, the Ni atom clusters deal are deposited from a porous Ni skeleton structure. In addition, the Ni atom clusters are synchronized with the NiAl\(_3\) single-phase corrosion, so that the morphology surface formed has no pore structure. The porous Ni skeleton size of \( \text{Ni}_{15}\text{Al}_{85} \) was 100~400nm. The small pore size is 5~20nm. The porous Ni skeleton size of \( \text{Ni}_{10}\text{Al}_{90} \) was 100~300 nm. The small pore size is 5~15 nm. \( \text{Ni}_{15}\text{Al}_{85} \) and \( \text{Ni}_{10}\text{Al}_{90} \) have the same composition, both of which are composed of Al phase and NiAl\(_3\) phase. Therefore, the corrosion mechanism is approximately the same, except for the difference of Al content. When these two alloys are placed in NaOH solution, Al phase and NiAl\(_3\) phase form the galvanic cell system, with Al phase as the anode and NiAl\(_3\) phase as the cathode. When the chemical reaction occurs between the alloy and NaOH etching solution, electron transfer also takes place in Al phase and NiAl\(_3\) phase galvanic cell systems. Al high activity, superior to NiAl\(_3\) phase reaction progress, makes up of Al large aperture structure formation, and NaOH etching liquid in contact with NiAl\(_3\) large area, make easy corrosion NiAl\(_3\) phase also dissolves in the Al atoms in the corrosive liquid, then NiAl\(_3\) phase of Ni atom atomic regrouped, form small pore size of the structure of the rough surface morphology. This is similar to the corrosion pattern of Cu\(_{15}\text{Al}_{85} \) in alkaline solution studied by WB Liu et al[20]. Qi et al. prepared Ni-Al alloys with three different components and dealloyed them in alkaline etching solution to obtain porous Ni[21]. The results showed that there was a genetic relationship between the microstructure of porous Ni after corrosion and the phase composition of precursor alloy[22].
It can be seen that the phase composition and active component content have great influence on the corrosion morphology in binary alloy system. In order to further analyze the microstructure of the dealloyed nanoporous Ni-Al alloy, the dealloyed nanoporous Ni was characterized by TEM and HRTEM. Figure 3(a) and (b) shows, the nanoporous Ni\textsubscript{25}Al\textsubscript{75} alloy obtained after dealloying has no fine pore structure. The lattice fringe of the high-resolution atlas was measured, and the crystal plane spacing was calculated to be 0.202nm, which was consistent with the (111) crystal plane spacing of the face-centered cubic structure Ni. Figure 3(c) and (d) shows, the nanoporous Ni skeleton structure obtained by dealloying Ni\textsubscript{15}Al\textsubscript{85} alloy is distributed with small pore structure, with the size ranging from 5~20 nm. The lattice stripes shown in the high resolution are clear, and the crystal plane spacing is calculated to be 0.181 nm, which is consistent with the (200) crystal plane spacing of the face-centered cubic structure Ni. Figure 3(e) and (f) shows, the porous Ni skeleton of Ni\textsubscript{10}Al\textsubscript{90} alloy obtained after dealloying is provided with holes with a size of 5~15nm, and the lattice fringes shown in the high resolution are clear. The surface spacing is calculated to be 0.206nm, which is consistent with the (111) crystal surface spacing of the surface centered cubic structure Ni. The diffraction pattern showed that the three nanoporous Ni were polycrystalline and had an amorphous trend[23].
Summarize three kinds of composition Ni-Al alloy corrosion mechanism, it can be seen that Ni_{25}Al_{75} alloy formation of nanoporous structure with single phase solid solution (such as Cu-Mg, Cu-Ni, Au-Ag [24-26]) alloy formation of nanoporous structure principle is the same, all is the same single corrosion reaction between liquid, remove lively group of Yuan, the inert group Yuan to reassemble the nanoporous structure, single structure, can't gather to form holes on the surface of the frame structure. Ni_{15}Al_{85} and Ni_{10}Al_{90} are two-phase galvanic cell systems, and the Al-rich phase and NaOH corrosion liquid react together to form a large pore structure by the corrosion of the Al-rich phase, and then form a small pore structure on the skeleton structure surface by the insoluble phase. Different components of Ni-Al alloy affect its phase composition, and phase composition is the leading factor in the formation of its corrosion morphology, so the corrosion morphology of Ni-Al alloy with different components has obvious differences.

Figure 4 shows the N\textsubscript{2} absorption and desorption curves of porous Ni from Ni_{25}Al_{75}, Ni_{15}Al_{85} and Ni_{10}Al_{90} with different components and the pore size distribution curves. It can be seen from the figure that the N\textsubscript{2} adsorption-desorption curves of the three kinds of porous Ni belong to class IV curves, and all of them have hysteresis rings, indicating that the porous Ni prepared contains mesoporous structure, and hysteresis rings are the capillary condensation phenomenon caused by the mesoporous structure. The specific surface areas of the three kinds of nano-porous Ni were 48 m\textsuperscript{2}⋅g\textsuperscript{-1} respectively, 101 m\textsuperscript{2}⋅g\textsuperscript{-1} and 140 m\textsuperscript{2}⋅g\textsuperscript{-1}. It can be seen that with the increase of Al content, the specific surface area of porous Ni increases, and a larger specific surface area can provide more active sites for electrocatalytic hydrogen evolution, which greatly improves the catalytic performance of electrode materials for hydrogen evolution.

3.2. Electrochemical activity analysis

Figure 5 shows the cathode polarization curve (LSV) measured by the nano-porous Ni/GCE electrode after dealloyed by Ni_{25}Al_{75}, Ni_{15}Al_{85} and Ni_{10}Al_{90} in 1mol⋅L\textsuperscript{-1} NaOH solution. It can be seen from
Figure 5 that the initial hydrogen evolution potential of the three cathode polarization curves is significantly different, and the initial hydrogen evolution potential represents the performance of each electrode in hydrogen evolution. Three types of nano porous Ni/GCE starting hydrogen evolution potential respectively is: a = 1.55 V, b = 1.48 V, C = 1.44V, Ni_{10}Al_{90} alloying of nano porous Ni/GCE off hydrogen evolution potential significantly lower than the other three electrodes, the nanoporous Ni/GCE electrode Ni_{25}Al_{75} income starting hydrogen evolution potential is 110mV.

![Figure 5. LSV curves of different Ni_{x}/GCE electrodes](image)

The relationship between overpotential and current density of Ni_{x}/GCE electrode in solution was tested, namely Tafel relationship:

\[
\eta = a + b \log i
\]  

(2)

Table 2 kinetic parameters of hydrogen evolution at different electrodes Results show that Ni_{10}Al_{90} has a high electrocatalytic performance of hydrogen evolution, and its apparent exchange current density at room temperature is 1.17 times that of Ni_{15}Al_{85} and 3.83 times that of Ni_{25}Al_{75}, respectively. The high exchange current density indicates that Ni_{10}Al_{90} has a faster electron transport speed, i.e. faster hydrogen evolution kinetics. BET test results can also further demonstrate the apparent exchange current density of the electrode. On the premise of constant energy factor, only geometric factors determine the hydrogen evolution performance of the electrode. Ni_{10}Al_{90} dealloying nanoporous Ni has the highest specific surface area, which, in contrast, has the highest electrochemical catalytic performance[27].

| Ni_{x}/GCE | a(V)   | b(V)   | i_0(A·cm^{-2}) |
|-----------|--------|--------|----------------|
| Ni_{25}Al_{75} | 8.496  | 1.888  | 3.162×10^{-5}  |
| Ni_{15}Al_{85} | 6.420  | 2.148  | 1.028×10^{-4}  |
| Ni_{10}Al_{90} | 2.368  | 0.812  | 1.210×10^{-4}  |

In order to further explore the electrocatalytic activity of the electrodes, the impedance spectra of the three electrodes at different overpotential were measured in this experiment. As shown in figure 6(a) for Ni_{25}Al_{75}, Ni_{15}Al_{85} and Ni_{10}Al_{90} of three kinds of alloy after alloying of nano-porous Ni/GCE electrode at room temperature electrochemical impedance diagram, can be seen from the figure in the three curves present a larger radius of circular arc, the line is a typical charge transfer resistance and electric double layer capacitors in parallel. And the radius shown in the curve decreases in turn. With the increase of specific surface area, the total hydrogen evolution resistance of the electrode decreases,
indicating that the hydrogen evolution overpotential decreases. Figure 6(b) shows the Nyquist plots and equivalent circuit diagrams of the nano-porous Ni/GCE electrodes obtained by dealloy-Ni₁₀Al₉₀ at different negative bias voltages, in which $R_{sl}$ is the solution resistance, CPE is the constant phase element, $R_{ct}$ is the charge transfer resistance, $C_{dl}$ is the double layer capacitance of the electrode, and $R_{w}$ is the electrochemical desorption resistance. As can be seen from Table 3, the solution resistance basically remains stable with little change. With the increase of negative bias voltage, $R_{ct}$ and $R_{w}$ show a trend of gradual decrease, and the overall resistance of the system becomes smaller. In figure 6(b), the radius of the arc decreases with the increase of negative bias pressure, indicating that the electrochemical resistance gradually decreases and the kinetic step of hydrogen evolution is accelerated.

![Figure 6. Electrochemical impedance spectra of nano-porous Ni/GCE](image)

| Potential (mV) | $R_{sl}/\Omega \cdot \text{cm}^2$ | $R_{ct}/\Omega \cdot \text{cm}^2$ | $R_{w}/\Omega \cdot \text{cm}^2$ |
|---------------|---------------------------------|---------------------------------|---------------------------------|
| 50            | 1.38                            | 60.76                           | 807.00                          |
| 100           | 1.36                            | 45.01                           | 623.80                          |
| 200           | 1.28                            | 13.27                           | 275.9                           |

Stability is very important for hydrogen evolution electrode. In practical production and application, stability restricts production efficiency and productivity. Figure 7 shows the cathodic polarization curves of three nanoporous Ni/GCE electrodes in wt(NaOH)= 25% solution with a voltage range of -0.8~0.6V (Vs.RHE) before and after 1000 cycles of cyclic scanning at a speed of 100mV. As can be seen from the figure, the stability of the nanoporous Ni/GCE electrode obtained after the dealloying of the three Ni-Al alloys was not significantly different, and the hydrogen evolution potential difference before and after the reaction was about 100mV. This also proves that the nanoporous Ni prepared by dealloying has good stability without obvious dissolution in alkaline solution.
Conclusions
In this paper, nano-porous Ni was successfully obtained via one-pot de-alloying with different atomic ratio of Ni-Al precursor. The results show that the specific surface area increased with the increase of the Al element. Ni10 exhibit a thick skeleton with small pores on the surface, which provide a large number of activity sites for HER. A low onset potential with -1.44 V was provided and a stationary chronoamperometry curve proved a remarkable durability. The nano-porous Ni with abundant channels and pores make it a very promising non-precious electrocatalyst for hydrogen production.

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