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Monoethanolamine Electro-Oxidation Assists Efficient Hydrogen Evolution over Nickel Nanowire Arrays Anode

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Abstract. In order to decrease the decomposition voltage of hydrogen evolution in ordinary alkaline or acidic water and simultaneously degrade the Ethanolamine (MEA) sewage, the efficient hydrogen evolution assisted by MEA electro-oxidation over nickel nanowire arrays anode is investigated in this work. The nickel nanowire arrays anode is successfully fabricated with the aid of the polycarbonate template and the low-melting point alloy. The electrochemical results show the driving voltage to deliver the same current density of 20 mA cm⁻² in the 1.0 mol L⁻¹ KOH/0.05 mol L⁻¹ MEA solution is lowered by 12.2% than that in 1.0 mol L⁻¹ KOH solution. The present study proves the viability to produce hydrogen efficiently by electrolyzing the MEA-containing water.

1. Introduction

Monoethanolamine (MEA) is a kind of organic material, which owns one amidogen and oxhydryl attaching to each of the two carbon atoms, respectively. MEA is frequently used as the absorbent for carbon dioxide and hydrogen sulfide in chemical industrial process, and the alkalizer to adjust the pH value of the water used in the firepower power station and nuclear power station. Owing to its extensive application in different domains, how to treat the MEA sewage becomes a severe environmental issue. On most occasions, MEA is degraded by adsorptive process, photocatalysis, activated sludge process and the chemical oxidation. However, for the perspective of cyclic utilization, those methods are wasting treasure since MEA can be utilized in the production of hydrogen--which is a vital substance in the energy field--concurrently while being degraded.

By virtue of the high hydrogen purity, hydrogen production by the electrolysis of water stands out among those by steam reforming of mineral fuel, by the gasification of biomass and etc. Nevertheless, one demerit that we must focus on is the high electrical energy consumption. Be more specific, the theoretical decomposition voltage for the electrolysis of water is 1.23 V, and the actual decomposition voltage would be much higher if accounting for the electrochemical, concentration and ohmic polarizations. In order to decrease the decomposition voltage, the electrolysis of hydrazine- or urea-containing water, instead of the electrolysis of ordinary acidic and alkaline water, is employed. Bao Yu Xia et al.[1] pointed out the potential needed to exert the electro-catalytic current density of 10 mA cm⁻² in hydrazine-containing water is merely -0.05 V vs. RHE, overwhelming that in ordinary alkaline water (~1.51 V vs. RHE). The drastic decrease in the onset potential of anodic electro-oxidation reaction



results in an ultra-low decomposition voltage of 0.164 V (@10 mA cm⁻²). Another example is in urea-containing water. Botte et al.[2] found that the current in the Huffman electrolytic cell was increased from 1 mA in ordinary alkaline water to 20 mA in urea-containing water when applied the decomposition voltage of 1.5 V, which implies the acceleration of hydrogen evolution.

Similarly, the addition of MEA in ordinary alkaline water may also favors the energy saving. Teresa Łuczak et al.[3] published a chemical sensor based on the electro-oxidation of MEA over gold nanoparticles. Results show the onset potential was as negative as -0.9 V vs. SCE. As to that occurring on the non-noble metal catalyst, say Cu-Ni alloys, the onset potential reached almost 0.3 V vs. SCE, still a lower value when compared with that in the water without MEA[4].

To reinforce the purpose of energy-saving, an anode catalyst with excellent catalytic performance is demanded. Although the noble metals often show better catalytic activity because of the unsaturated electron couple in the d-orbital, the high price hinders their extensive use. Especially, the latest price of palladium has gone up to 1540.55 US\$ per troy oz[5]. To this end, the non-noble metals should be employed.

In this work, we report an easy-manipulation and low-cost method to fabricate the self-supported nickel nanowire arrays (Ni NAs) electrode. The open 3-dimensional structure and abundant active sites endow the electrode with remarkable activity toward the electro-oxidation of MEA. Far more than this, the present studies lay theoretical fundamentals for electrochemical degradation of MEA and hydrogen evolution in MEA-containing water.

2. Experimental section

2.1. preparation of nickel nanowire arrays

The polycarbonate filter (~50 nm for the pore diameter) was used as the template for nickel nanowire array electrodeposition. The low-melting point bismuth alloy (55°C) was brushed onto one surface of the template in the oven (90°C), and once solidified the alloy acted as the current collector. The electrodeposition happened in the traditional Watt nickel plating bath, where the solidified template-alloy worked as the anode and the electrolytic nickel sheet as the cathode. Extra conditions included appropriate stirring, heating remained at 55 °C for the bath and applied current density of -40 mA cm⁻² lasting about 4 hours. This electrodeposition MEASURE yielded a self-supported nickel nanowire arrays (Ni NAs) since nickel electrodeposition firstly took place in the pore and then occurred on the other surface of the template. Finally, the template coupled with the nickel electrodeposits was peeled down from the alloy, and the template was dissolved in warm KOH aqueous solution to free the nanowires. The use of low-melting point alloy avoids the operation of gold spray onto the surface of template, which thereby simplifies the preparation procedure and lowers the cost.

2.2. Material characterization and electrochemical tests

The morphology of the Ni NAs electrode was observed by scanning electron microscopy (SEM, Hitachi S-4300, Japan). Three-electrode or two-electrode electrochemical tests were conducted in KOH or KOH/MEA aqueous solution controlled by the electrochemical station (CHI 660E). The working, counter and reference electrodes were Ni NAs, Pt sheet and Ag/AgCl electrodes, respectively. The reference electrode was taken out for the two-electrode system. The solution was deaerated by bubbling the N₂ gas for 20 min, and then the N₂ atmosphere was maintained above the electrolyte during testing.

3. Results and discussion

Figures 1(a) and (b) are the SEM images of Ni NAs at low and high magnifications, respectively. The nanowire arrays are standing on the support and forming the morphology of barley which has been shaken by the wind. The "ravine" between the "barley" offers highway for the rapid diffusion of reactants and products. Since the electro-catalysis here is a heterogeneous reaction, the specific surface area of the catalyst plays a significant role in the reaction rate. The structure of nanowire, with the diameter no

more than 100 nm, provides abundant active sites; hence the electro-oxidation of MEA will be greatly facilitated.

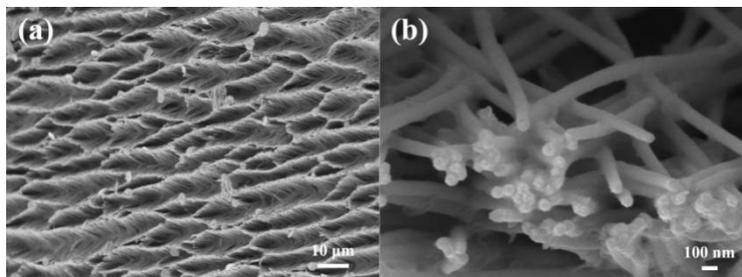


Figure 1. SEM images of Ni NAs at low (a) and high (b) magnifications.

Figure 2(a) displays the cyclic voltammetric (CV) curves of Ni NAs in the 1.0 M ($M = \text{mol L}^{-1}$) KOH with and without 0.01 M MEA, respectively. The redox peaks between ~ 0.35 V in KOH solution represent the $\text{Ni(OH)}_2/\text{NiOOH}$ conversion reaction. Interestingly, we find the onset potential of electro-oxidation of MEA is identical to that of $\text{Ni(OH)}_2/\text{NiOOH}$ conversion reaction, inferring that the electro-oxidation of MEA is triggered by the superficial NiOOH of the Ni NAs. As reported previously, urea, ethanol, methanol and glucose electro-oxidation on the nickel catalyst shared the same characteristic with the MEA electro-oxidation. Those put forward the following E-C coupling mechanism[6]:



Where Equation (1) is an electrochemical reaction and Equation (2) is a chemical reaction, respectively. The MEA electro-oxidation here may follow such reaction mechanism as well. According to Equation (1), the OH^- concentration affects the formation of NiOOH, which was proved in Figure 2(b). When the OH^- concentration increases from 0.5 to 5 M, the onset potential shifts negatively from 0.39 to 0.29 V vs. Ag/AgCl. Figure 2(c) shows the CV response (the backward data were eliminated for convenient observation) when the concentration of MEA is altered from 0 to 0.2 M. We evaluate the optimal MEA concentration based on the two criteria: onset potential and current density. Here the onset potential is read at the point when the current density is 1.0 mA cm^{-2} , and the current density is read when the potential is 0.55 V. Two plots of E_{onset} vs. C_{MEA} and j vs. C_{MEA} are demonstrated in Figure 2(d). As seen, the j gradually increases from 0 to 0.05 M; however it decreases from 0.05 to 0.2 M. It is manifested that not all the large reactant amounts favor the proceeding of electro-oxidation reaction. The variation trends of E_{onset} and j suggest 0.05 M is the optimal MEA concentration. The stability of MEA electro-oxidation on the Ni NAs electrode is evaluated by chronoamperometry (CA) method. The CA curves under 0.4, 0.5 and 0.6 V kept relatively stable, and slight current drop may blame on the consume of MEA and/or the sluggish concentration diffusion in the mainstream (Figure 2(e)).

The electrochemical impedance spectroscopy (EIS) is also utilized to probe the mechanism of MEA electro-oxidation. As shown in Figure 3, the Nyquist plots under the OCP show spikes closely to 90° , inferring the capacitive ad-/de-sorption behaviour at the solid-liquid interphase. Once at 0.35 V and 0.43 V, both the Nyquist plots in KOH and in KOH/MEA solution deliver the arc-shape, which illustrates the occurrence of MEA electro-oxidation. The smaller diameter of the arc indicates the faster electro-oxidation reaction. Because the addition of MEA enhances the $\text{Ni(OH)}_2/\text{NiOOH}$ conversion reaction, the arcs in KOH/MEA become smaller than those in KOH solution. According to Figure 2(c), higher potential provides larger driving force for the electrochemical reaction, thus smaller arc is witnessed as the polarization potential increases from 0.35 V to 0.43 V. When the polarization potential is 0.54 V, the arc falls into the second, third and fourth quadrant as with the gradual descending frequency. Such

sophisticated EIS data are usually observed in electrochemical corrosion system and seldom in electrocatalytic system. But based on the previous studies about urea electro-oxidation, the odd phenomenon may stem from the strong adsorption of the intermediates [7].

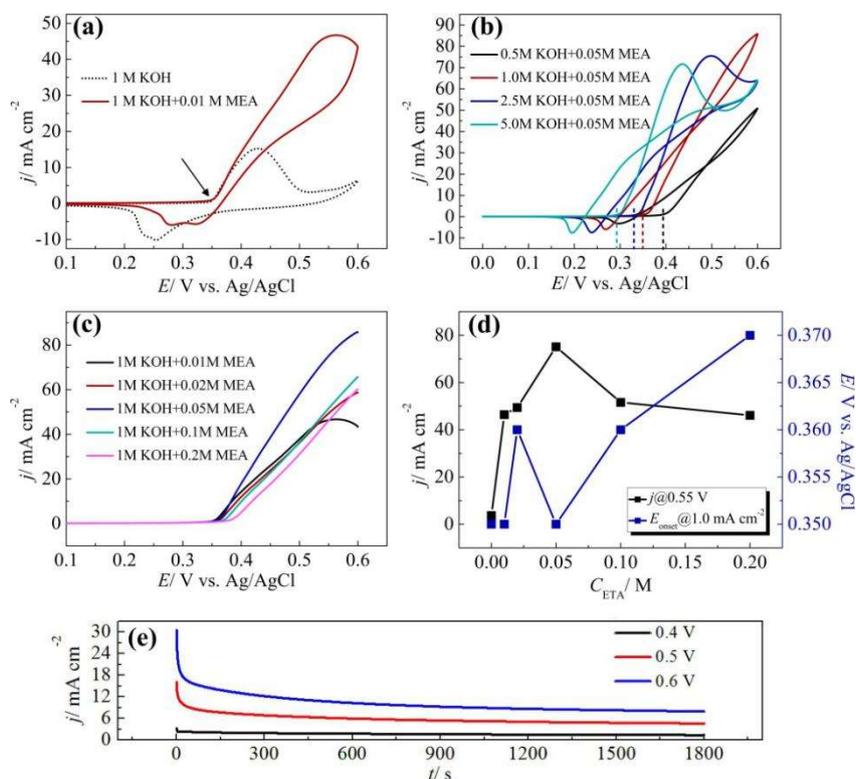


Figure 2. (a) CV curves of Ni NAs in 1.0 M KOH and 1.0 M KOH/0.01 M MEA, respectively; (b) CV curves of Ni NAs in x M KOH/0.05 M MEA ($x=0.5, 1.0, 2.5$ and 5.0); (c) half CV curves of Ni NAs in 1.0 M KOH/ x M MEA ($x=0.01, 0.02, 0.05, 0.1$ and 0.2); (d) plots of E_{onset} vs. C_{MEA} and j vs. C_{MEA} ; (e) CA curves of Ni NAs at 0.4, 0.5 and 0.6 V. Scan rate for CV and LSV is 10 mV s^{-1} .

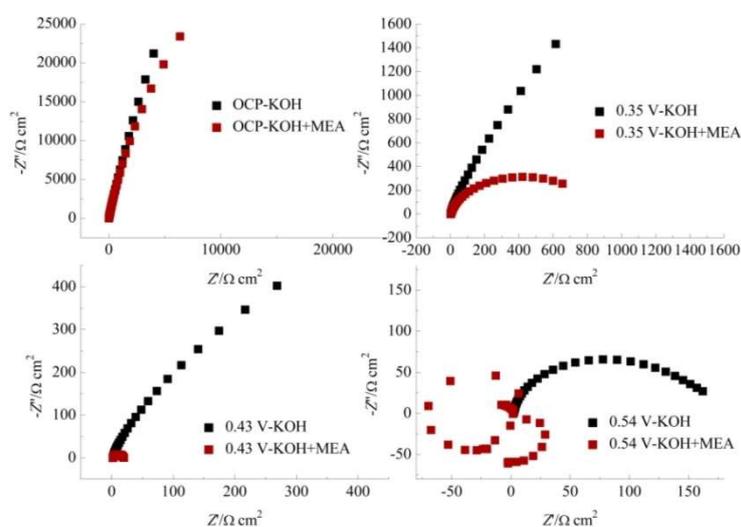


Figure 3. Nyquist plots of Ni NAs at the OCP, 0.35 V, 0.43 V and 0.54 V in 1.0 M KOH and 1.0 M KOH/0.05 M MEA, respectively. Potential amplitude is 5.0 mV and frequency range is $10^{-2} \sim 10^5$ Hz.

The Pt sheet was used as the cathode catalyst for hydrogen evolution reaction (HER) in KOH and KOH/MEA solutions, respectively. The linear sweeping voltammetric (LSV) curves in Figure 4(a) evidently show the addition of MEA doesn't affect the velocity of HER: almost the same onset potential and current density. Although the onset potential of KOH/MEA solution equals to that of bare KOH solution, the driving force to deliver the current density of 20 mA cm^{-2} is very different. As marked by the two dashed horizontal lines, the decomposition voltage used in KOH/MEA is 1.62 V, almost 240 mV lower than that in bare KOH solution. In such case, the electric energy consumption can be reduced by 12.2%. Figure 4(b) presents the decomposition voltage variations with time under the current density of 20 mA cm^{-2} . The decomposition voltage in KOH/MEA solution always locates under that in bare KOH solution, and at 1800s the difference in the decomposition voltage reaches 162 mV.

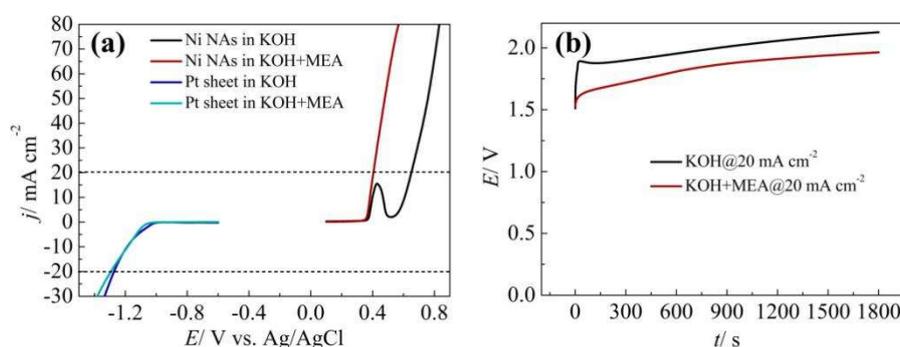


Figure 4. LSV curves of Ni NAs and Pt sheet (a), and decomposition voltage variations with time under the current density of 20 mA cm^{-2} (b) in 1.0 M KOH and 1.0 M KOH/0.05 M MEA, respectively. Scan rate for LSV is 10 mV s^{-1} .

4. Conclusion

The electrochemical results show the driving voltage to deliver the same current density of 20 mA cm^{-2} in the 1.0 M KOH/0.05 M MEA solution is lowered by 12.2% than that in 1.0 mol L⁻¹ KOH solution. The present study proves the viability to produce hydrogen efficiently by electrolyzing the MEA-containing water. However, further efforts should be exerted to promote the hydrogen production performance in MEA-containing water.

Acknowledgments

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