

Preparation of Non-noble Metals Supported on Carbon by Polymer Templatation Method for Solid Alkaline Fuel cells

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ABSTRACT

One of the most important cost items is platinum which is used as catalyst both in anode and cathode sides of exchange membrane fuel cells. Not only is the cost of the platinum, but also the limited reservoir of the platinum is handicap. Therefore, the utilization of the cheap replacements of platinum will accelerate the process of commercialization. NiCoFe (NCF), NiCo (NC), and NiFe (NF) are group of the non-noble metals electrode catalyst for alkaline fuel cell. The NCF, NC, and NF were synthesized by mixing Ni, Co, and Fe complexes into polymer matrix (melamine-formaldehyde), followed by heating the mixture at 800 °C for 1 h under inert atmosphere. XRD, SEM, EDX, TEM, and SAD experiments suggest that all prepared samples have both alloy and oxide form.

Keywords – Non-noble metals, Polymer templatation method, Solid alkaline fuel cells, NiCoFe, NiCo, NiFe

1. INTRODUCTION

Fuel cells, as devices for direct conversion of the chemical energy of a fuel cell into electricity by electrochemical reactions, are one of the key technologies for effective use of energy. Recently, alkaline fuel cell (AFC) has regained attention because an alkaline media provides a less corrosive environment to the catalysts and electrodes than the acid environment of a polymer electrolyte fuel cell (PEMFC) [1-4]. Also, the electrodes can be made of nonprecious metal electrodes [5-6]. In order to reduce the cost of the alkaline fuel cell catalyst, two approaches are following up: a) exploration of non-noble catalyst, and b) reduction of the Pt loading. So, it is important to develop nonprecious metal electrode catalysts for AFC [7]. In recent years, a few nonprecious metal electrode catalysts for AFC were found. P-M-C complex materials were prepared by polymer template coordination with metal-ions loaded with a carbon-reduction method. P stands for polymer; M = Fe, Co, and Ni; C is carbon. The catalyst showed very high electrocatalytic activity for oxidation in alkaline media [8]. Acta has developed Fe/Co/Ni binary and ternary catalysts by polymer templatation method which works with

hydrogen and hydrocarbon fuel [9]. Also, it has been reported that a direct ethanol fuel cell carbon-supported Ni-Co-Fe catalyst as the cathode is capable of selectively reducing oxygen without oxidation of ethanol deriving from the anode.

In the present works, NiCoFe/C, NiCo/C, and NiFe/C catalysts is to prepare by polymer templatation method. The metals supported on carbon are synthesized by the first reacting a melamine with formaldehyde in solution, in the present of a catalyst, carbon particles and a metal salt, at temperature and time which sufficient to provide a polymerized product. Then the product is heated to provide the form of a powder.

2. EXPERIMENTAL

2.1 Materials and methods

All the chemicals used were of analytical grade (Aldrich) except carbon black and NaOH which were supplied by Cabot and Volchem, respectively. X-ray diffraction (XRD) was used to identify the sample. This analysis was performed by a Bruker D5005 power diffractometer. Diffraction patterns were produced by employing CuK_α radiation at 35 mA and 35 kV, and scan speed of 0.3 degree/0.02 second. A JSM-5410V scanning electron microscope (SEM) with INCA software by Oxford for energy dispersive X-ray spectroscopy (EDS) was used to estimate the element composition of different regions of the product. For SEM and EDS samples preparation, samples were dropped on conductive carbon tape which attached to SEM stubs. The micrographs were recorded with an acceleration voltage of 15 kV at 5000x magnification. The morphology and structure of all products were also characterized by transmission electron microscope, JEOL model JEM-2010 operating at 20 kV. The sample were prepared by dispersing a small amount of sample in absolute ethanol and put same droplets of the solutions onto copper grids coated with holey carbon films and letting the ethanol evaporate slowly under a lamp.

2.2 Preparation of non-noble metals supported on carbon

The non-noble metals supported on carbon were prepared reported previously by Park,

Bianchini, and Witherspoon [10-12]. The amount of formaldehyde used was about 0.01 g and 50 mL of water mixed with 12.61 g of melamine, and the mixture was heated at 60 °C for 10 min. Then 0.5 g of nickel (II) acetate tetrahydrate, 0.5 g of cobalt (II) acetate tetrahydrate, 0.5 g of iron (II) acetylacetonate (for the case preparation of ternary non-noble metals composite: NiCoFe; NCF), 5.0 g of carbon black (Vulcan XC-72R), 0.45 mL concentrated HCl aq. solution and 15 mL of water, were added to the mixture under stirring. The mixture was mechanically stirred for 20 h at 90 °C to give gel like composite materials. The gel was heated in a furnace at 800 °C under inert atmosphere for 1 h. Similarly, binary non-noble metals composite (NiCo; NC, NiFe; NF) of Ni, Co, and Fe were also prepared. Our strategy for preparation of NiCo and NiFe are similar to the case of the NiCoFe composited was made. Two different preparation were chosen, first, NiCo composites metal used only nickel (II) acetate tetrahydrate and cobalt (II) acetate tetrahydrate of 0.5 g. Secondly, the amount of nickel (II) acetate tetrahydrate 0.5 g and iron (II) acetylacetonate 0.5 g were used for preparation of NiFe binary non-noble metals. Schematic procedures for NCF, NC, and NF preparation are shown in Fig.1.

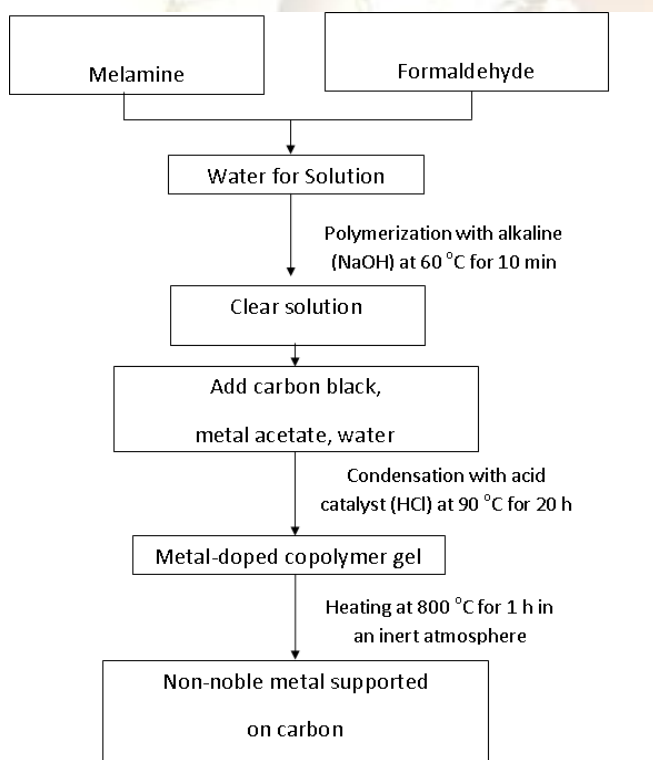


Fig.1. Preparation procedure of non-noble metal supported on carbon

3. RESULTS AND DISCUSSION

Powder X-ray diffraction (XRD) was first introduced to analyze non-noble metals supported on carbon in order to identify the elemental composition

and their structure type. Fig. 2 shows XRD patterns of NiCoFe/C, NiCo/C, and NiFe/C heated at 800 °C for 1 h. XRD patterns of iron oxide based samples are shown in Fig.2 (a), and 2 (c), which indicates a typical crystal graphic structure of Fe₂O₃ (220) at $2\theta = 30.241$, (311) at $2\theta = 35.631$, (400) at $2\theta = 43.285$, (422) at $2\theta = 53.734$, (511) at $2\theta = 57.273$, and (440) at $2\theta = 62.927$ according to JCPDS number 00-039-1346. Also, the peaks are found at $2\theta = 62.167$ (220), $2\theta = 74.515$ (311), and $2\theta = 78.443$ (222) according to JCPDS number 01-070-2855, can be assigned to structure of CoO (fig. 2 (b)). Further, with the $2\theta = 37.254$ (111), indicate the characteristic peaks for NiO (Fig. 2(a), (b), and (c)). For all non-noble metals show the peaks assigned to NiCoFe alloy (43.3, and 75.3), NiCo alloy (43.2, 48.9, and 74.8), and NiFe alloy (43.8, 51.0, and 75.6) accordance with the method reported by Nakamura and Coworkers [13-14]. All samples from polymer templation method were observed corresponded to metal oxide and metal alloy. Therefore, the TEM, SEM, EDS, and SAD were then applied to identify the occurrence of these samples.

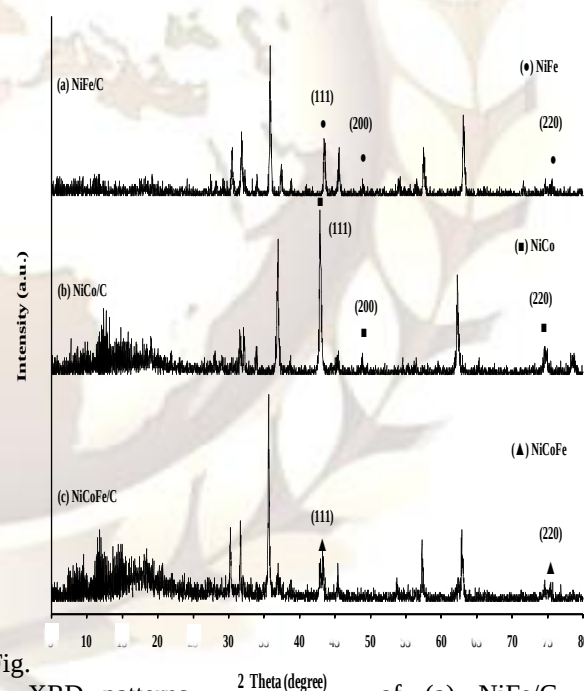


Fig. 2. XRD patterns of (a) NiFe/C, (b) NiCo/C, and (c) NiCoFe/C

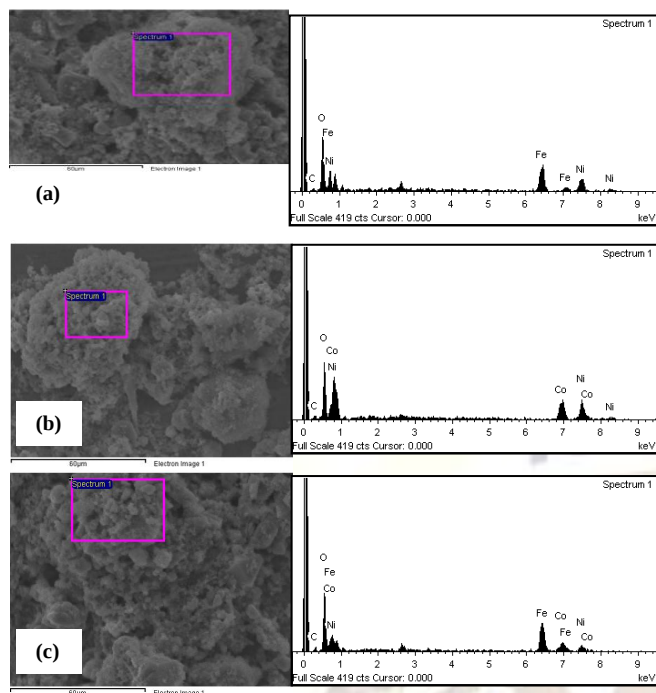


Fig. 3. SEM photograph and EDX profiles of (a) NiFe/C, (b) NiCo/C, and (c) NiCoFe/C

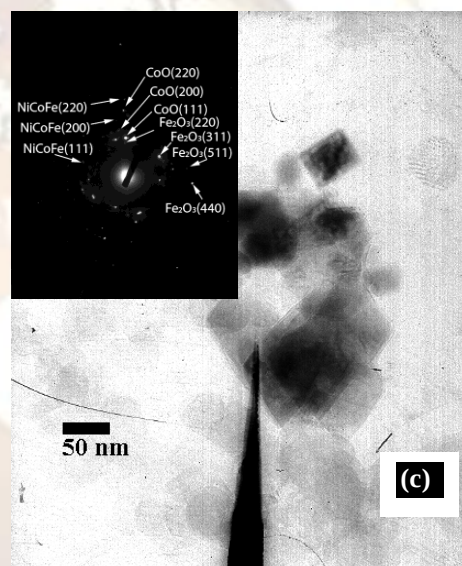
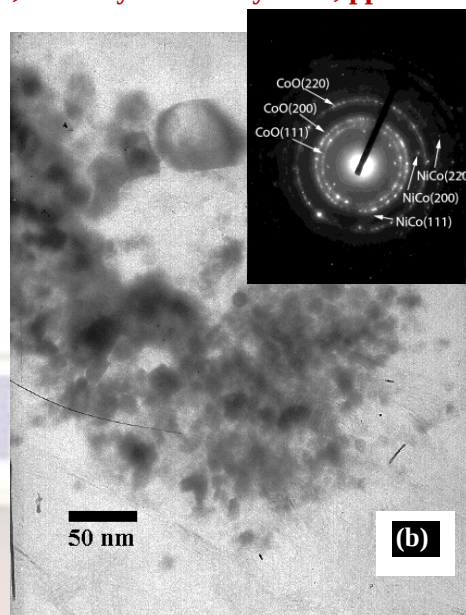
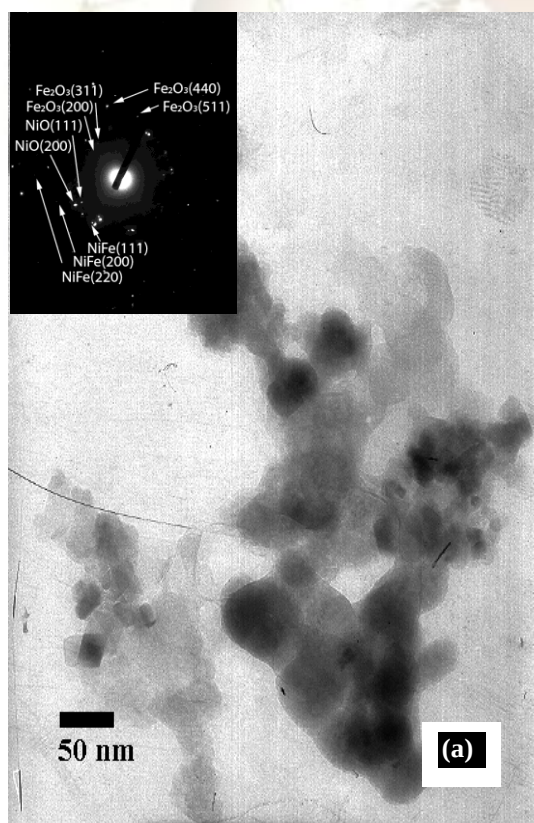


Fig. 4. TEM images and SAD patterns of (a) NiFe/C, (b) NiCo/C, and (c) NiCoFe/C



The surface morphology of the samples is investigated by SEM and the composition of the surface elements were analyzed with EDS. The SEM micrographs of the obtained NiCoFe/C, NiCo/C, and NiFe/C are shown in Fig. 3 with 5000 times of magnification. The SEM micrographs show porous structure of carbon black particles with various sizes. EDX spectra of the carbon-supported NiCoFe, NiCo, and NiFe confirm the presence of respective elements and a large amount of oxygen, which are assigned to peaks of oxides. The average composition of elements in the NiCoFe, NiCo, and NiFe are found to be approximately 1 : 1 : 1.5, 1 : 1, and 1 : 1 : 1.5, respectively. TEM images of metal supported on carbon as shown in Fig. 4, which gave the particle size distribution of particles on carbon supporters is about 5- 50 μm . SAD patterns of Fe_2O_3 , NiO, and

CoO based catalyst displayed the crystallographic structure of Fe_2O_3 , NiO, and CoO which corresponded to their XRD patterns. The SAD patterns of NiCoFe, NiCo, and NiFe alloy exhibited diffraction rings be almost the same as (110), (200), and (211) corresponding to XRD pattern. Considering the XRD and TEM results, it is suggested that the polymer templating method can successfully synthesize NiCoFe, NiCo, and NiFe supported on carbon.

4. CONCLUSION

The NiCoFe/C, NiCo/C, and NiFe/C were prepared by polymer templation method. First, reacting melamine with formaldehyde in solution, in the presence of a catalyst (NaOH), carbon black and metals acetate, at 90 °C for 20 h sufficient to provide a polymerized product in the form of metal-doped copolymer. Then the product is heated to 800 °C in an inert atmosphere for 1 h to provide the form of a powder as metal support on carbon. These powders can be used as catalyst for alkaline fuel cells and electrochemical measurement for further experimental.

5. ACKNOWLEDGEMENTS

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