

Ni-based Catalyst Supported on Mesostructured Silica Nanoparticles (MSN) for Methanol Oxidation Reaction (MOR)

(Mungkin Berasaskan Ni Disokong oleh Silika Nanopartikel Mesostruktur (MSN) untuk Tindak Balas Pengoksidaan Metanol)

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ABSTRACT

A new catalyst based on mesostructured silica nanoparticle (5wt%, 20wt%, and 30wt% Ni-MSN) were prepared by the wet impregnation method and used for electro-oxidation of methanol. While, MSN as a catalyst support was synthesized using co-condensation and sol-gel method. The synthesized MSN and Ni-MSN were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and Fourier Transform Infra-red (FTIR) techniques. Ni-MSN catalysts were successfully prepared by mixing with the conducting graphite in 1:1 ratio which called carbon paste electrode (CPE). Mixing with graphite, in this work, was particular necessary to increase the electrical conductivity of the Ni-MSN materials. For fuel cell applications, the electrochemical measurements for methanol oxidation were investigated using cyclic voltammetry (CV) and chronoamperometry (CA) in 1.0 M NaOH and 1.0 M CH₃OH for modified electrode, Ni-MSNCPE. Among the three samples, 30wt% Ni-MSNCPE exhibits a high current density (~ 8 mA cm⁻²) and long-term chronoamperometry stability (3600 s) toward methanol oxidation in alkaline solution. This may attribute to the high dispersion of nickel and ordered mesoporous structure which can facilitate the diffusion of methanol and products. 30wt% Ni nanoparticles supported onto MSN catalyst demonstrate better electrocatalytic activity and stability than the 5wt% and 20wt% Ni-MSNCPE catalysts.

Keywords: Mesostructured Silica Nanoparticle; anode catalyst; methanol oxidation reaction; modified electrode

ABSTRAK

Mungkin baru berasaskan mesostruktur silika nanopartikel (5wt%, 20wt%, and 30wt% Ni-MSN) disediakan dengan menggunakan kaedah pengisitepuan basah dan digunakan untuk pengelektrooksidan metanol. Manakala, MSN sebagai mungkin sokongan disintesis menggunakan kaedah kondensasi bersama dan sol-gel. MSN dan Ni-MSN yang disintesis dicirikan dengan menggunakan pembelauan sinar-X (XRD), mikroskop imbasan elektron pancaran medan (FESEM), dan Infra Merah Jelmaan Fourier (FTIR). Mungkin Ni-MSN telah berjaya disediakan dengan mencampurkan grafit yang bersifat konduksi dengan nisbah 1:1 yang dikenali sebagai elektrod pes karbon (CPE). Percampuran dengan grafit, dalam kerja ini, sangat diperlukan untuk meningkatkan kekonduksian elektrik bahan Ni-MSN. Untuk aplikasi sel fuel, pengukuran elektrokimia bagi pengoksidaan metanol dikaji menggunakan voltametri berkitar (CV) dan kronoamperometri (CA) di dalam 1.0 M NaOH dan 1.0 M CH₃OH untuk elektrod yang diubah suai, Ni-MSNCPE. Antara ketiga-tiga sampel, 30wt% Ni-MSNCPE menunjukkan ketumpatan arus yang tinggi (~ 8 mA cm⁻²) dan kestabilan jangka panjang kronoamperometri (3600 s) terhadap pengoksidaan metanol di dalam larutan alkali. Ini mungkin disebabkan oleh penyebaran nikel yang tinggi dan struktur berliang meso yang tersusun yang memudahkan resapan metanol dan hasil. Mungkin 30wt% Ni nanopartikel yang disokong ke MSN menunjukkan aktiviti dan kestabilan elektromungkin yang lebih baik berbanding mungkin 5wt% dan 20wt% Ni-MSNCPE.

Kata kunci: Mesostruktur silika nanopartikel; mungkin anod; tindak balas pengoksidaan methanol; elektrod diubah suai

INTRODUCTION

In recent years, direct methanol fuel cells (DMFCs) have garnered great attention as power sources due to their several advantages of using methanol as a fuel which has low operating temperature and better safety, higher energy density (3800 kcal/l) than hydrogen (658 kcal/l used as the

fuel in proton exchange membrane fuel cells), and ease of handling methanol (than H₂) (Zainoodin, Kamarudin & Daud 2010). However, their commercial success is yet to be proven and significantly depends on two factors: the high cost associated with precious metal electrocatalysts (for example, Pt) and enhancements in the catalytic activity at the anode (Kamarudin et al. 2006; Patel et al. 2015; Ting et

al. 2016; Zhao et al. 2011). Thus, the great progress towards non Pt-based has been made recently. The usability of non Pt-based catalyst have received intensive research attention in alkaline medium because of a less corrosive environment. Besides that, it also can improved reaction kinetics (L. Wang et al. 2016), enhanced kinetics of electrocatalytic oxidation of methanol at low anodic overpotential (Antolini & Gonzalez 2010), and reduced the adsorption of CO intermediates that might limit electrocatalysis (Peng, Sun & Asiri 2015). Nevertheless, it still remains an enormous challenge to develop low-cost anodic catalysts with superior activity and stability to replace Pt-based catalysts (Liu, Chen & Zhu 2016).

Nickel-based anode catalyst is one of the alternatives promising catalyst to Pt-based catalysts because of it has high electrocatalytic activity performance, good stability, and low poisoning effect as well as reduced cost. Particularly, Ni-based catalysts, such as metallic Ni (Rahim 2004), Ni alloy (Danaee et al. 2010), Ni(OH)₂ (El-Shafei 1999) and NiO (Tong et al. 2016), are the most extensively studied Ni-based catalysts in alkaline DMFCs. The role of Ni in all previous studies shows that it has good surface oxidation properties to increase the electrocatalytic activity. In 2014, Hassan et al. (Hassan et al. 2014) prepared Ni-MCM41 catalysts for methanol oxidation reaction (MOR) in alkaline medium. He found that Ni catalyst has very small or negligible poisoning effect as it contains many pores and channel which permit easier removal of the oxidation products.

Catalyst support material plays a vital role to improve the fuel cell performance; carbon-based and silica-based materials have been widely investigated as support material for anode catalyst in DMFCs. Therefore, it is important to select suitable support material to enhance the performance of the catalyst. At present, mesostructured silica nanoparticle (MSN) has attracted great fundamental and applied research efforts due to its excellent properties such as large surface area (> 1000 m² g⁻¹), thermal and mechanical stability, highly uniform pore size distribution, tunable pore size, high adsorption capacity and excellent dispersibility in aqueous media as a support material for the catalyst in DMFCs (Karim et al. 2012; Karim et al. 2014). However, MSN has low electrical conductivity and resulted in high electrical resistance in the reaction, which affects the performance of methanol oxidation. Thus, to increase the electrical conductivity of the catalysts, carbon paste electrode (CPE) that so-called modified electrode is introduced.

So far no work has been reported on the application of Ni/MSN modified electrode as anodes catalysts for DMFC applications. In this paper, Ni catalyst supported on MSN was prepared using wet impregnation method. Then, the synthesized electrocatalysts were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) and Fourier transform Infra-red (FTIR). Electro-oxidation of methanol is investigated using cyclic voltammetry (CV) and chronoamperometry (CA) techniques. This work will provide

a promising solution to replace the Pt-based catalysts as anodes for alkaline DMFCs in order to reduce costs.

METHODOLOGY

SYNTHESIS OF MSN

MSN was synthesized using co-condensation and sol-gel method according to the previous report (Aziz et al. 2014; Karim et al. 2014). Briefly, CTAB surfactant (4.68 g), EG solvent (120 ml) and NH₄OH solution (29 ml) were dissolved in 720 ml of DI water. After vigorous stirring for approximately 30 min at 323 K, TEOS (5.7 ml) and APTES (1.052 ml) were added to the clear mixture to give a white suspension solution. This solution was stirred for an additional 2 h at 353 K. The resulting mixture allowed to rest for 24 h in the refrigerator until it completely separates into two layers. Then, the samples were collected by centrifugation at 5000 rpm for 10 min and washed with DI water and absolute ethanol (1:1) 5 times. The synthesized MSN were dried overnight at 383 K and calcined at 823 K for 3 h to remove the surfactant.

SYNTHESIS OF NI/MSN

Ni/MSNs electrocatalyst were prepared by the wet impregnation method (Aziz et al. 2014; Aziz et al. 2014). The aqueous nickel nitrate (Ni(NO₃)₂·6H₂O) were impregnated on the support (MSN) at 353 K. Then, the sample was dried in the oven at 383 K overnight before calcination in air at 823 K for 3 h.

ELECTRODE PREPARATION

Electrocatalytic inks were prepared by mixing 30 mg of the catalyst and 30 mg graphite powder with 200 µL of 5wt.% Nafion[®] 117 and 800 µL 2-propanol, and then the resultant mixture was dispersed in an ultrasonic bath for 2 h. 2.5 µL of the resulting ink was then pipetted onto glassy carbon electrode (GCE) surface, but before that, the electrode was polished well with 0.05 µm alumina pastes followed by ultrasonic cleaning in DI water. The electrode dried at 80°C for 1 h before measurement.

PHYSICAL AND ELECTROCHEMICAL CHARACTERIZATION

X-ray diffractometer (XRD) analysis was performed with a model Bruker D8 Advance at 40 kV with CuKα radiation (λ = 0.15406 nm). The diffraction angle, 2θ was recorded from 2 – 80° to analyze the crystallinity and crystal phase of catalysts. The morphology of dispersion Ni on MSN was studied using field emission scanning electron microscopy (FESEM Model No. SUPRA 55 VP) and to determine the elements contained in the samples is using EDX, which was attached to the FESEM. To identify the chemical functional groups present in the samples, Fourier Transform Infrared (FT-IR) spectroscopy (Perkin Elmer GX FTIR spectrometer) was carried out. The catalyst was finely ground and dispersed

into KBr powder-pressed pellets with a ratio of 1 mg sample to 200 mg KBr. The electrocatalytic activity of the Ni/MSN catalysts towards MOR was evaluated by cyclic voltammetry (CV) in a conventional three-electrode cell. A glassy carbon electrode (GCE) with an area of 0.07068 cm^2 was used as working electrode, a Pt rod was used as the counter electrode, and Ag/AgCl was used as reference electrode. CV experiments were performed in a solution containing electrolyte which is 1.0 M NaOH in 1 M CH_3OH as fuel at a scan rate of 50 mVs^{-1} . Similar experiments were performed for chronoamperometry (CA) measurements. CA measurements were done at -0.2 V for 3600 s.

RESULTS AND DISCUSSION

STRUCTURAL PROPERTIES

Figure 1A shows the small angle XRD pattern for the MSN and Ni-MSN in the range $2\theta = 2 - 10^\circ$. The patterns demonstrated three main diffraction peaks shown in the Fig. 1A at $2\theta = 2.3, 4.1,$ and 4.7° relative to the (1 0 0), (1 1 0), and (2 0 0) reflections respectively, which indexed to a p6mm hexagonal structure of mesoporous silica, displaying the high quality of the mesopore packing (Aziz et al. 2014). The ordered MSN support structure was not disturbed by the inclusion of Ni. No shifts in the peaks of the small-angle XRD patterns were observed, but the intensities decreased slightly with the introduction of Ni, indicating minor structural degradation of MSN. The presence of metal crystallites of NiO supported on MSN were characterized using wide-angle XRD patterns ($20 - 80^\circ$), as shown in Figure 1B, in which the diffraction peaks at $37.4, 43.4, 62.6, 75.4,$ and 79.4 can be attributed to a face-centered cubic crystalline NiO (Aziz et al. 2014). The peaks were more intense with the increasing Ni loading 5wt%, 20wt%, and 30wt%, corresponding to a more crystalline phase of NiO on the MSN support. The inconsistency in NiO crystal size among the catalysts was mainly due to the surface area of the MSN. Besides, the porous structure of MSN affects the particle size of Ni (Aziz et al. 2014).

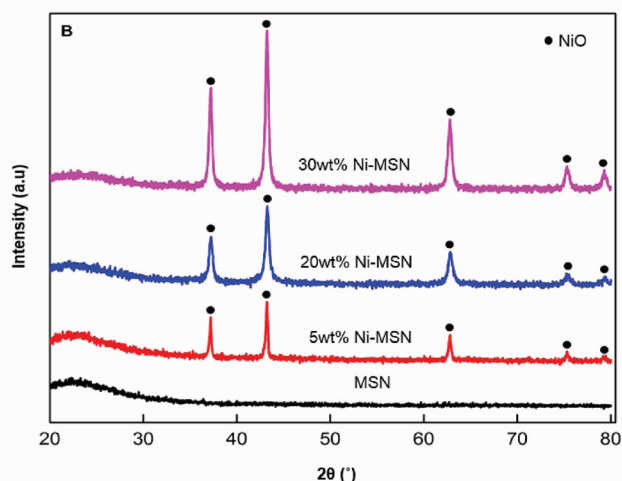
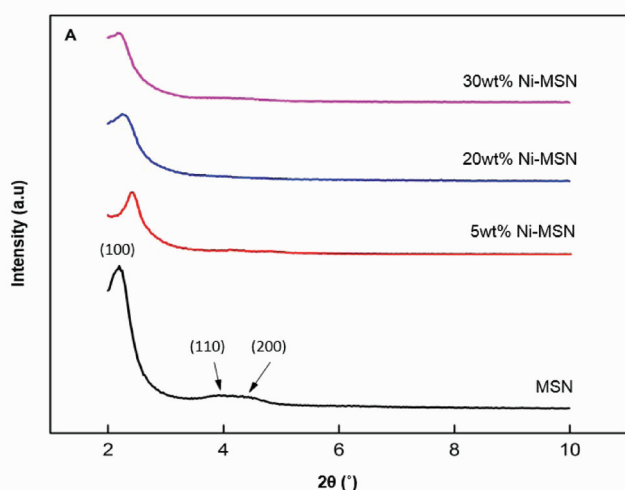


FIGURE 1. Small-angle (A) and wide-angle (B) XRD patterns of MSN, 5wt%, 20wt%, and 30wt% Ni-MSN electrocatalysts

MORPHOLOGICAL CHARACTERIZATION

Figure 2 (A-D) display micrographs of MSN, 5wt%, 20wt% and 30wt% Ni-MSN electrocatalysts with the magnification of 50kX. FESEM micrograph (a) reveals a fairly uniform ordered spherical particles of pure MSN with average diameter of 100 nm, which is consistent with the XRD result (Figure 1). The morphologies of Ni-MSN composites with different loading are shown in Figure (B) to (D). It can be seen that the spherical shape of the MSN was sustained with of Ni loaded onto MSNs and the metal particles have filled up some of the pores (Madzaki et al. 2018). But the shape of MSN was slightly reduced and less aggregated when the Ni was introduced (Jusoh et al. 2015). The spherical particles with large pores as a catalyst support contributed to an enhanced performance by reducing diffusion limitations, thereby improving the material's electrocatalytic activity for the MOR.

FTIR CHARACTERIZATION

To confirm the structural changes between the MSN sample and Ni-MSN composites, FT-IR analysis was performed and the results are shown in Figure 3. All Ni-MSNs displayed similar FT-IR spectra with typical patterns of MSN, consisting of bands at $462, 806, 970, 1085, 1646,$ and 3418 cm^{-1} . From the IR peaks at the bands ascribed is Si-O-Si (462 cm^{-1}), Si-O-Si symmetric stretching (806 cm^{-1}), external Si-OH groups (970 cm^{-1}), Si-O-Si asymmetric stretching (1085 cm^{-1}), water molecules retained by siliceous materials (1646 cm^{-1}) and $-\text{OH}$ stretching (3418 cm^{-1} , broad) (Aziz et al. 2014; Karim et al. 2012; Karim et al. 2014). The relative intensity of the IR bands for transmittance is different could be due to the different morphology of the nickel particles (Aziz et al. 2014). Accordingly, the intensity of IR bands decreased when the Ni loading increasing was caused by the presence of a bulk Ni phase.

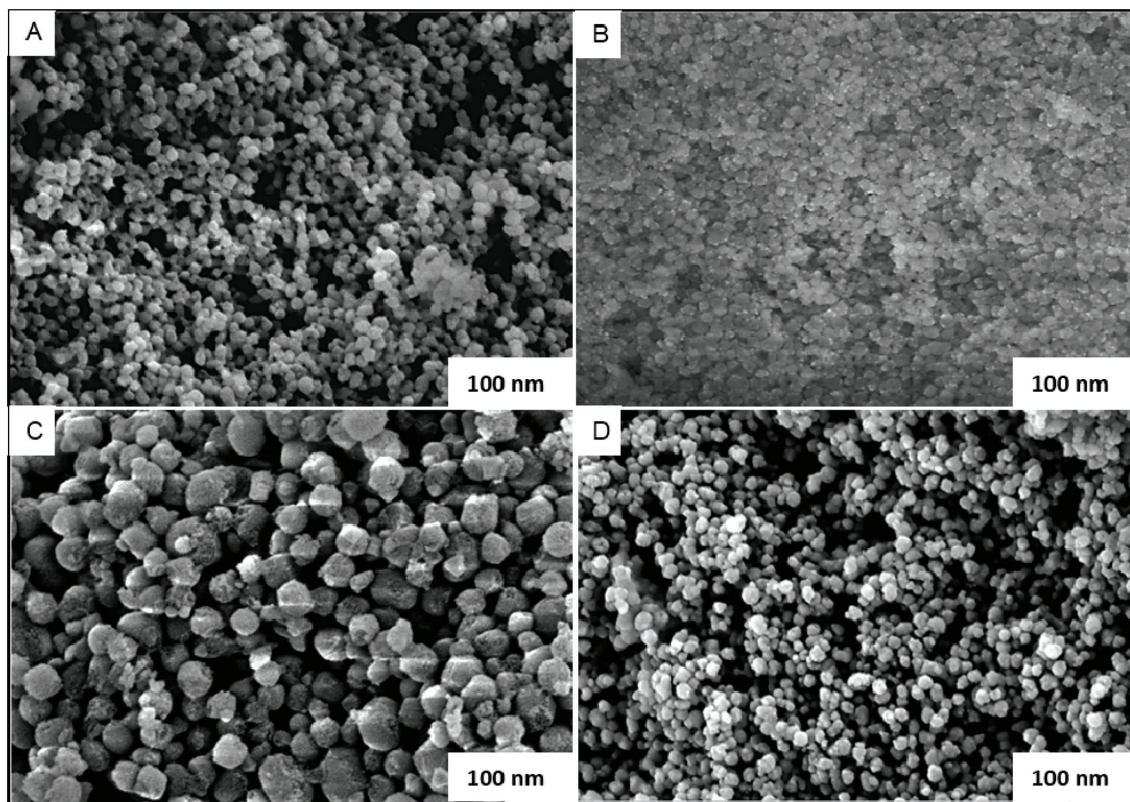


FIGURE 2. FESEM images of MSN (A), 5wt% (B), 20wt% (C), and 30wt% (D) Ni-MSN electrocatalysts with magnification 50 KX

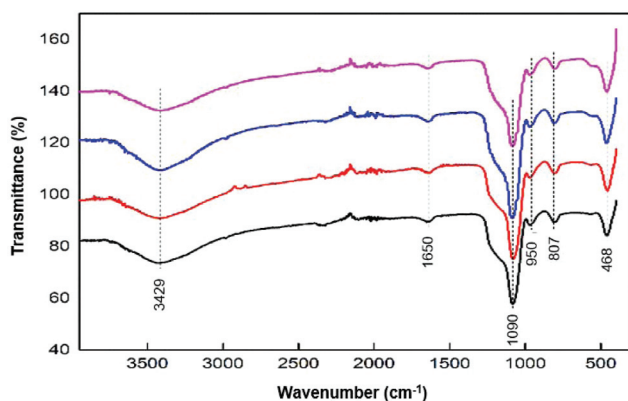
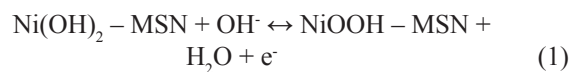


FIGURE 3. FTIR spectra of MSN, 5wt%, 20wt%, and 30wt% Ni-MSN electrocatalysts

ELECTROCHEMICAL CHARACTERIZATION

The cyclic voltammograms of Ni-MSNCPE with different loading of Ni in 1.0 M NaOH solution at potential range from -1.0 to 0.5 V versus Ag/AgCl at a scan rate of 50 mV/s is shown in Figure 4. According to the electrochemical behavior of nickel electrode in the alkaline electrolyte, at potential range from -0.4 to 0.4 V, the conversion of α -Ni(OH)₂ to β -Ni(OH)₂ take place (Rahim 2004). 5wt% Ni-MSNCPE sample does not show any obvious peak. In voltammograms in Figure 4, hydrogen evolution takes place at the starting potential

characterized by a high anodic current. For sample 20wt% Ni-MSNCPE, it can be seen two obvious peaks in the anodic and cathodic direction which at 0.49 and 0.42 V respectively. While the peak at 0.44 V in the anodic directions and another peak at 0.36 V in the cathodic directions for sample 30wt% Ni-MSNCPE. This couple of peak attribute to the oxidation of Ni(OH)₂ to NiOOH in accordance with the following reaction in equation 1 (Azizi et al. 2013; Azizi et al. 2013; Rahim 2004):



The peak at the negative potential side consists of a small anodic peak at a potential value of -0.47 V that corresponds to the oxidation of nickel according to the reaction:



The addition of 1.0 M methanol to the electrolyte made some changes in the voltammetric behavior of the electrode. Figure 5 represents the electrochemical oxidation of 1.0 M CH₃OH in 1.0 M NaOH at a scan rate of 50 mV/s. An anodic peak for methanol electrooxidation was taken place with the NiOOH formation starts to be formed at the onset potential. This indicates the NiOOH species are the active species for methanol electrooxidation. The potential values for 20wt% and 30wt% Ni-MSNCPE are -0.17 and -0.03 V, respectively. Another oxidation peak for methanol oxidation can be seen in

the reverse scan but a much smaller value of current density. This peak most likely due to the reoxidation of methanol and/or the intermediate products resulting from the methanol oxidation reaction (Hassan et al. 2014). Among Ni-MSNCPCE with different Ni loadings, 30wt% Ni-MSNCPCE displays the highest current density ($\sim 8 \text{ mA cm}^{-2}$). In comparison with other studies, wang et al. (Y. Wang et al. 2017) get the peak current density at 7.3 mA cm^{-2} for Ni/Al₂O₃ which is comparable with this study. No obvious current density peak of methanol oxidation on CV of 5wt% Ni-MSNCPCE could be observed, which indicates 5wt% Ni-MSNCPCE is not a sufficient enough of Ni loading for the electrocatalyst to disperse in mesoporous structure resulted in no electrocatalytic activity in methanol oxidation reaction.

Figure 6 represents chronoamperometry curves for the 5wt%, 20wt% and 30wt% Ni-MSNCPCE in 1.0 M NaOH + 1.0 M CH₃OH at a constant potential -0.2 V for 3600 s. This test was carried out to compare the long-term stability of the catalysts towards methanol oxidation reaction. In all of the obtained current density vs. time curves, there was an initial drop in the first 500 s (possibly due to the charging current), followed by a slower decay. The 30wt% Ni-MSNCPCE electrocatalyst was most active compared with 5wt% and 20wt% Ni-MSNCPCE. During the initial and steady current densities of 30wt% Ni-MSNCPCE electrocatalyst 9 times higher than 20wt% Ni-MSNCPCE in the entire time range used. After a long duration of the reaction, the current gradually decreased for all the catalysts but 30wt% maintained a slightly higher current than the other catalysts. For all the catalysts, the current density values decayed with time because of the formation intermediates species due to the applied potential is not positive enough to completely oxidize the reaction intermediates (Hassan et al. 2014). So, it can be concluded that the presence of MSN as a catalyst support for Ni can enhance the resistance to deactivation caused by the intermediates, resulting in enhanced stability.

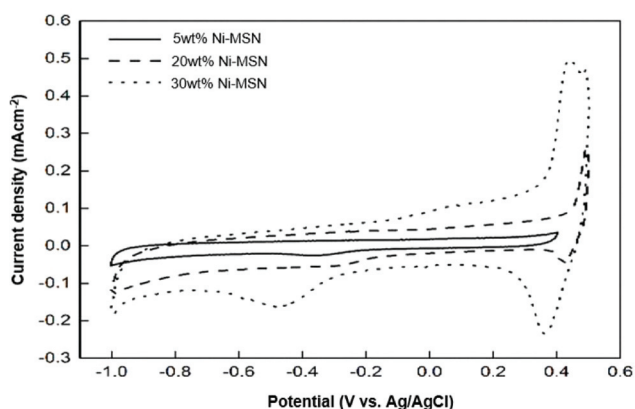


FIGURE 4. Cyclic voltammograms of the 5wt%, 20wt%, and 30wt% Ni-MSNCPCE electrocatalysts in 1.0 M NaOH solution saturated with nitrogen at a scan rate of 50 mV/s.

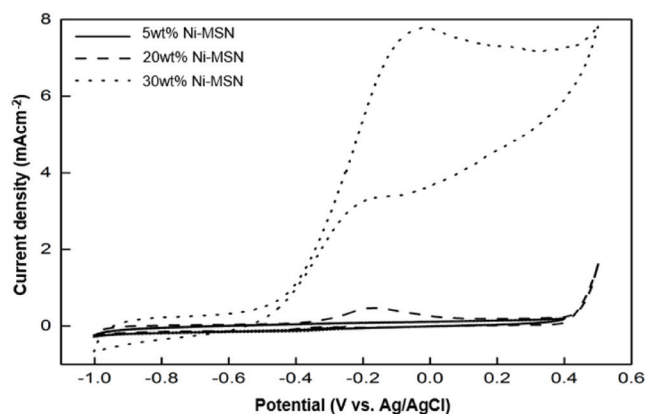


FIGURE 5. Cyclic voltammograms of the 5wt%, 20wt%, and 30wt% Ni-MSNCPCE electrocatalysts in 1.0 M NaOH + 1.0 M CH₃OH solution saturated with nitrogen at a scan rate of 50 mV/s

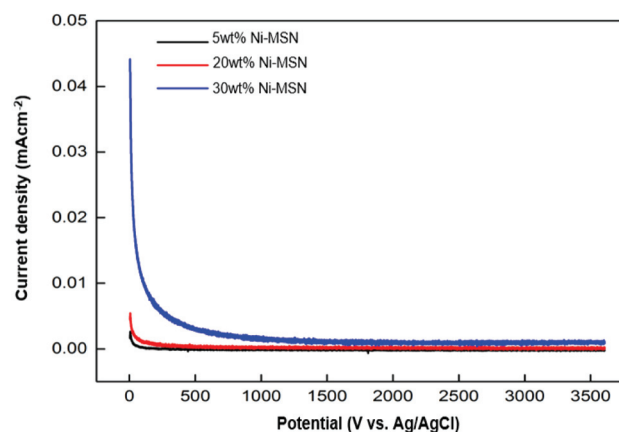


FIGURE 6. Chronoamperometry of the 5wt%, 20wt%, and 30wt% Ni-MSNCPCE electrocatalysts in 1.0 M NaOH + 1.0 M CH₃OH solution saturated with nitrogen at E = -0.2 V

CONCLUSION

In this work, 5wt%, 20wt%, and 30wt% Ni/MSN catalysts were prepared by the wet impregnation method. XRD results indicate that Ni/MSN catalysts obtain a high quality of the mesopore packing and hexagonal structure of mesoporous silica. FESEM results show that an ordered mesostructured of pure MSN and highly porous structure of MSN. When Ni is load onto MSN the particle size was reduced. Based on FTIR results, it could be suggested that the intensity of IR bands decreased when the Ni loading increasing was caused by the presence of a bulk Ni phase. As a catalyst for methanol oxidation in alkaline medium, 30wt% Ni-MSNCPCE reveals a higher current density $\sim 8 \text{ mA cm}^{-2}$, most stable (3600 s), which surpass many state-of-art Ni-based catalysts. The remarkable catalytic performance of the 30wt% Ni-MSNCPCE electrocatalyst is due to its unique structure, morphology, and composition.

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