Ni(II) decorated nano silicoaluminophosphate molecular sieves-modified carbon paste electrode as an electrocatalyst for electrooxidation of methanol

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MS received 11 April 2015; accepted 3 December 2015

Abstract. In this work, we reported a method for the synthesis of nanosized silicoaluminophosphate (SAPO) molecular sieves that are important members of zeolites family. The synthesized SAPO was characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) as well as infrared (IR) techniques. Then, the modified carbon paste electrode was prepared by nano SAPO molecular sieves and nickel (II) ion incorporated at this electrode. The electrochemical behaviour of the modified electrode (Ni-SAPO/CPE) towards the oxidation of methanol was investigated by cyclic voltammetry and chronoamperometry methods. It has been found that the oxidation current is extremely increased by using Ni-SAPO/CPE compared to the unmodified Ni-CPE, it seems that Ni²⁺ inclusion into nano SAPO channels provides the active sites for catalysis of methanol oxidation. The effect of some parameters such as scan rate of potential, concentration of methanol, amount of SAPO was investigated on the oxidation of methanol at the surface of modified electrode. The values of electron transfer coefficient, charge-transfer rate constant and electrode surface coverage for the Ni(II)/Ni(III) couple in the surface of Ni-SAPO/CPE were found to be 0.555, 0.022 s⁻¹ and 5.995 × 10⁻⁶ mol cm⁻², respectively. Also, the diffusion coefficient and the mean value of catalytic rate constant for methanol and redox sites of modified electrode were obtained to be 1.16 × 10⁻⁵ cm² s⁻¹ and 4.62 × 10⁴ cm³ mol⁻¹ s⁻¹, respectively. The good catalytic activity, high sensitivity, good selectivity and stability and easy in preparation rendered the Ni-SAPO/CPE to be a capable electrode for electrocatalytic oxidation of methanol.

Keywords. Nano SAPO; molecular sieves; modified electrode; electrocatalytic oxidation; methanol.

1. Introduction

Direct methanol fuel cells (DMFCs) as power sources for electronic devices are attractive for storage and apply in portable power generator [1]. In the DMFC, methanol is used as a fuel so it is important that to improve electrocatalytic oxidation of methanol so that decrease in the large over voltages that are encountered in its direct oxidation at most unmodified electrode surfaces [2]. Also, methanol as the fuel has many benefits such as simple operation, high energy density and low price, but the relatively slow kinetics of the methanol oxidation reaction leads to high overpotentials [3]. Therefore, there is much attention in developing new materials for the electrocatalytic oxidation of methanol in alkaline medium [4]. The use of alkaline solutions in a fuel cell has many advantages such as increasing its efficiency and a wider choice of possible electrode materials, no sensitivity to the surface structure and negligible poisoning [5,6].

The modified electrodes containing transition metals as catalytic sites can be utilized as electrocatalytic membranes to evaluate the concentrations of several species. Their catalytic performances have developed advantages in the immobilization of an appropriate molecule for various applications [7]. Among these electrode materials currently used in electrochemistry, the carbon paste electrode (CPE) was described in the literature since 1958 by Adams [8]. This research area was actively advanced particularly in the manufacturing of new carbon paste modified electrodes by immobilizing the desired compounds to improve their electrochemical performances in many applications such as in catalysis and electrochemical sensors [7,9]. The choice of this material as electrode can be justified by several advantages such as simple and easy fabrication, no easily poisoned, renewable surface, low price with an acceptable stability [8].

Electrode materials for methanol oxidation need to have high electrocatalytic efficiency. Different electrode materials based on Pt electrodes were generally used as catalysts for the methanol electrooxidation [10]. Nickel is a relatively

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abundant and low price material that is utilized widely in numerous industrial applications. It is well established that Ni can be used as a catalyst based on its surface oxidation properties and has long-term stability in the alkaline solutions [11]. Many of the electrodes involved nickel as a component. The pure nickel or nickel-based electrodes have been used for the electrooxidation of alcohols [4,11–15]. Different forms of nickel electrodes such as nickel foam [16], nickel nanoparticles [17] and nickel-cermet electrode [18] have been studied for methanol electrooxidation.

These catalysts need to have the highest possible surface area. Therefore, supported electrodes are generally used as catalysts. Zeolites are materials with high surface area that reaches several hundred square meters per gram [19]. Research on porous materials such as zeolites has increased considerably because of their high potential applications in the fields of catalysis [20], sensing [21], gas storage [22] and adsorbent [23]. The more pore entries, the more available active sites for contacting with reactants, consequently higher catalytic activity. Briefly, small size of crystals shortens the length of products and decreases the diffusion resistance, leading to an improved electrocatalytic oxidation [24]. Silicoaluminophosphate (SAPO) molecular sieves are important members of zeolites family. There are several routes for synthesis of SAPO with small crystals by taking advantage of using different templates, silicon sources, molar compositions, organic base solvents and crystallization conditions [25]. These experimental suggest that control of SAPO molecular sieves' size is a crucial factor in improving the electrocatalytic activity and lifetime of the electrocatalyst [26]. Metal or metal oxide clusters have been introduced into zeolite cavities mostly by ion-exchange [27] or solution impregnation procedure [28].

The modified electrode based on zeolite and mesoporous materials such as Ni-ZSM-5 [29,30], Ni-SBA-15 [31], Ni-SBA-16 [32], Ni-analcime [33] and nickel phosphate [20,34] have been used for electrocatalytic oxidation of methanol. In respect of the literature survey, no SAPO molecular sieves were utilized for modification of carbon paste electrode towards electrocatalytic oxidation of methanol. In this study, SAPO molecular sieves with nanodimension was synthesized and characterized. Then, nano SAPO molecular sieves were utilized for modification of carbon paste electrode and applied for electrocatalytic oxidation of methanol in the alkaline medium.

2. Experimental

2.1 Materials

Tetraethylorthosilicate (TEOS), aluminium isopropoxide ($\text{Al}(\text{OPr}^i)_3$), sodium hydroxide (NaOH), tetraethylammonium hydroxide (TEAOH), potassium chloride (KCl), potassium hexacyanoferrate ($\text{K}_4\text{Fe}(\text{CN})_6$), phosphoric acid (H_3PO_4), methanol and nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were of analytical reagent grade and were purchased from Merck

Company and used without further purification. Graphite powder and paraffin oil (density 0.88 g cm^{-3}) as the binding agents (both from Daejung Company) were used for preparing the pastes. Also double distilled water was used throughout the experiment.

2.2 Preparation of SAPO molecular sieves

The SAPO molecular sieves were synthesized by conventional heating from the reaction mixture of $1 \text{ Al}(\text{OPr}^i)_3 : 2 \text{ H}_3\text{PO}_4 : 2 \text{ TEAOH} : 0.3 \text{ SiO}_2 : 75 \text{ H}_2\text{O}$ [35]. In a typical synthesis, $\text{Al}(\text{OPr}^i)_3$ was first mixed with TEAOH solution (20 wt% in water) and deionized water at room temperature until dissolves completely. Then, the TEOS as silica source was added and stirred for 2 h. Finally, H_3PO_4 (85 wt% in water) was dispersed slowly into the above solution. The reaction mixture was further stirred for 1 h until a homogeneous gel was obtained. The gel was transferred in a Teflon lined stainless steel and heated at temperature of 453 K for crystallization time of 24 h under static condition. The product was separated by high-speed centrifugation (1000 rpm), washed thoroughly with deionized water and ethanol, and then dried overnight at 50°C. The as-synthesized crystals were calcined at 550°C in air for 8 h to remove the TEAOH template molecules [36].

2.3 Apparatus

XRD pattern was recorded by X-ray diffractometer (XRD, GBC—MMA) with Be-filtered $\text{CuK}\alpha$ radiation. Scanning electron microscopy (SEM, VEGA2—TESCAN) was employed to study morphology and size of obtained crystal. The IR spectrum was obtained by a Bruker FT-IR spectrometer (Vector 22). The electrochemical experiments were performed at room temperature using potentiostat/galvanostat electrochemical analyzer (Ivium, The Netherlands, V11100) with a voltammetry cell in a three electrodes configuration. The $\text{Ag}|\text{AgCl}|\text{KCl}$ (3 M) and platinum wire were utilized as reference and auxiliary electrodes, respectively. The unmodified carbon paste electrodes (CPE) and modified carbon paste electrodes with SAPO molecular sieves (SAPO/CPE) were used as working electrodes.

2.4 Preparation of working electrode

For preparation of (SAPO/CPE), an appropriate amount of SAPO nano molecular sieves (10–30 wt% with respect to graphite) were mixed with suitable amount of graphite powder and then paraffin oil (35 wt%) was blended with the mixture in a mortar by hand mixing for 30 min until a uniformly wetted paste was obtained. This paste was packed into the end of a glass tube (ca. 3.5 mm i.d. and 10 cm long), with a copper wire as electrical contact. A new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper. For comparison, modified CPE

(bare CPE) in the absence of SAPO was also prepared in the same mentioned method.

3. Results and discussion

3.1 Characterization of nano SAPO molecular sieves

Figure 1 displays XRD powder pattern of the obtained SAPO molecular sieves. It shows that the position of the diffraction peaks of sample matches well with that of the simulated XRD pattern of the zeolite AFI framework. Izadbakhsh *et al* [37] reported that the higher intensity may indirectly explain the larger size of crystals and crystals in nanoscale always have broaden peaks. Comparison of the main peaks at $2\theta = 7, 19.44, 21.76, 22.56$ and 25.6° with the reference sample [37,38] indicated that the AFI phase (SAPO-5) was ascertained. Also, small value of CHA phase (SAPO-34) was discovered that was characterized in the XRD pattern and shown by a star. It must be emphasized when TEOS used as the silicon source, it can be hydrolyzed and produced alcohol which was proved to have structure directing effect on the formation of nano SAPO molecular sieves [39]. The crystallite size (D_c) of synthesized SAPO was also calculated using Debye–Scherrer equation [40]:

$$D_c = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where K is the shape factor which usually takes a value about 0.9, λ the wavelength of the X-ray source used in XRD (0.15418 nm), β the breadth of the observed diffraction line at its half-intensity maximum in radian and θ the main Bragg

Figure 1. Representation of XRD pattern of synthesized SAPO molecular sieves.

peak angle. According to the obtained results from XRD pattern, β is 0.303° at $2\theta = 22.56^\circ$. The crystallite size (D_c) of SAPO molecular sieves was about 26.75 nm.

The field emission scanning electron microscopy (FESEM) image of crystalline phase provides useful approach that can determine the size and morphology of the obtained crystals. Figure 2 shows SEM image of synthesized SAPO molecular sieves, which indicates that the formation of semi-spherical nanosized particle can be observed with dimension of $39 \times 33 \times 51$ nm.

The FTIR spectrum of nano SAPO molecular sieves in the range of $400\text{--}4000\text{ cm}^{-1}$ is shown in figure 3. The peak around 490 cm^{-1} is ascribed to the bending vibration of SiO_4 that characteristics to the Si which incorporated into the tetragonal structure of SAPO [41]. The peak nears 630 cm^{-1} is identified to bending vibration of SAPO catalyst and related to D_6 -ring in molecular sieves structure. The peaks at

Figure 2. Representative FESEM images of nanocrystalline SAPO molecular sieves.

Figure 3. FTIR spectrum of synthesized SAPO molecular sieves.

wavenumbers about 720, 1100 and 1650 cm^{-1} were assigned to the asymmetric stretch of O–P–O, symmetric stretch of O–P–O and physically adsorbed water, respectively [25]. The broad bands at 3000–3700 cm^{-1} centered at 3450 cm^{-1} is attributed to the stretching vibration of water molecules adsorbed on hydroxyl groups [26]. This spectrum is in agreement with the interpretation of obtained XRD results.

3.2 Electrochemical behaviour of modified electrode

Cyclic voltammetry (CV) was used for investigation of electrochemical properties of fabricated bare CPE and SAPO molecular sieves modified CPE (SAPO/CPE) in potassium ferricyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) solution. Figure 4 illustrates the cyclic voltammograms of the electrochemical oxidation of $\text{Fe}(\text{CN})_6^{4-}$ at the surface of the bare CPE (curve a) and SAPO/CPE (curve b) in the 10 mM $\text{K}_4\text{Fe}(\text{CN})_6$ plus 0.1 M KCl solution. As can be seen in this figure, the anodic and cathodic peak currents for SAPO/CPE is higher than that of at bare CPE. The experimental results show reproducible anodic and cathodic peaks ascribed to $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple at slow scan rates at the surface of SAPO/CPE. This is a quasi-reversible system because the peak separation potential, $\Delta E_p (E_{pa} - E_{pc})$, is equal to 160 mV and is greater than 59 mV that expected for a reversible system and this value was lower than that of at the surface of bare CPE (i.e., 260 mV). Also, it was obtained that the electrochemical behaviour of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple in the SAPO/CPE electrode is not dependent on pH of the solution.

The active surface areas of the fabricated electrodes were calculated by the CV method at various scan rates using $\text{K}_4\text{Fe}(\text{CN})_6$ as a probe. For this approach, the following Randles–Sevcik formula can be used [42–44].

$$I_{pa} = 0.4463AC_0(F^3/RT)^{1/2} n^{3/2} D_R^{1/2} \nu^{1/2}, \quad (2)$$

Figure 4. Cyclic voltammograms of (a) bare CPE and (b) SAPO/CPE in the presence of 10 mM $\text{K}_4\text{Fe}(\text{CN})_6$ solution plus 0.1 M KCl at a scan rate of 20 mV s^{-1} and pH of 7. Inset shows plots of I_{pa} vs. $\nu^{1/2}$ for the oxidation of 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.1 M KCl as supporting electrolyte in the surface of bare CPE and SAPO/CPE.

where I_{pa} (A) refers to the anodic peak current, A (cm^2) the active surface area of the electrode, C_0 (mol cm^{-3}) the concentration of $\text{K}_4\text{Fe}(\text{CN})_6$, F Faraday's constant (96485 C mol^{-1}), R the universal gas constant (8.314 $\text{J mol}^{-1} \text{K}^{-1}$), T the absolute temperature (298 K), n the electron transfer number, D ($\text{cm}^2 \text{s}^{-1}$) the diffusion coefficient and ν (V s^{-1}) the scan rate. For 1.0 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.1 M KCl as supporting electrolyte, the amount of n and D_R are 1 and $7.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$, respectively [42–44]. Inset in figure 4 illustrates plot of I_{pa} vs. $\nu^{1/2}$ for bare CPE and SAPO/CPE electrodes in 1.0 mM $\text{K}_4\text{Fe}(\text{CN})_6$ plus 0.1 M KCl. In this experiment, the slopes were obtained to be $6.337 \times 10^{-5} \text{ A (V}^{-1} \text{s}^{-1})^{1/2}$ and $17.322 \times 10^{-5} \text{ A (V}^{-1} \text{s}^{-1})^{1/2}$ for the bare CPE and SAPO/CPE, respectively. Therefore, the active microscopic surface areas were found to be 0.085 and 0.233 cm^2 for the fabricated CPE and SAPO/CPE electrodes, respectively. These results indicated that modification of CPE with SAPO molecular sieves causes to increase the active surface area of the electrode and linear plot of I_{pa} vs. $\nu^{1/2}$ indicates a diffusion control process at the surfaces of both electrodes.

3.3 Electrochemical behaviour of electrodes in alkaline solution

Inset in figure 5 shows CVs of bare CPE and SAPO/CPE in 0.1 M NaOH solution at the potential sweep rate of 20 mV s^{-1} . This figure indicates that no current can be achieved with these electrodes and the background current for SAPO/CPE is much larger than that of at bare CPE. The inclination of the base line for the voltammogram of SAPO/CPE electrode

Figure 5. Cyclic voltammograms of (a) bare CPE and (b) SAPO/CPE in the presence of 0.1 M NaOH at scan rate of 20 mV s^{-1} after immersed in 0.5 M NiCl_2 solution. Inset shows cyclic voltammograms of bare CPE (a) and SAPO/CPE (b) before immersed in 0.5 M NiCl_2 solution.

can be attributed to the additional resistance obtained from the presence of SAPO molecular sieves and the oxidation–reduction process of oxygen species in molecular sieve layer [45]. In the next step, the CPE and SAPO/CPE electrodes were immersed in a well-stirred aqueous solution of 0.5 M NiCl_2 at an open circuit for 10 min at 150 rpm and then washed completely with distilled water to remove the surface adsorbed species. Figure 5b illustrates CV of Ni-SAPO/CPE (SAPO/CPE that immersed in the 0.5 M NiCl_2) in 0.1 M NaOH solution and scan rate of 20 mV s^{-1} . It can be deduced that the electrochemical behaviour of Ni-SAPO/CPE modified electrode in alkaline solution is similar to that of Ni anode [11,20,46]. These redox waves are ascribed to the oxidation of Ni(OH)_2 at the SAPO/electrolyte interface to NiOOH and reduction of NiOOH to Ni(OH)_2 at a scan rate of 20 mV s^{-1} with a peak potential of 0.60 and 0.36 V vs. Ag|AgCl|KCl (3 M), respectively [11,20]. The broad cathodic peak can be ascribed to the phase transformation of $\beta\text{-NiOOH}$ to $\gamma\text{-NiOOH}$ due to slow, irreversible overcharging during cycling, and the corresponding reduction to $\alpha\text{-Ni(OH)}_2$ that this phenomenon originally reported by Bode *et al* [47].

After loading nickel ions on the surface of the electrodes, the anodic and cathodic peak currents for Ni-SAPO/CPE were much greater than those at Ni/CPE (see figure 5, curves a and b). These observations can describe clearly the role of

the SAPO nano molecular sieves on enhancement of the oxidation currents. Diffusion of Ni^{2+} ions in SAPO molecular sieve is much faster owing to their coordination to the framework of molecular sieves, the bigger cages and channels and fast migration of Ni^{2+} ions from the cages [20,48]. These redox waves are ascribed to the oxidation of Ni(OH)_2 at the SAPO/electrolyte interface to NiOOH and reduction of NiOOH to Ni(OH)_2 with a peak potential of 0.60 and 0.36 V vs. Ag|AgCl|KCl (3 M), respectively.

The surface of fabricated CPE, SAPO/CPE and Ni-SAPO/CPE electrodes were analysed by FESEM technique (see figure 6a–c). As seen on the surface of bare CPE in figure 6a, the layer of irregular flakes of graphite powder was present and isolated from each other. After addition of SAPO molecular sieves to the carbon paste, it can be seen that the SAPO was completely distributed on the surface of the electrode indicating that the SAPO was successfully incorporated into the CPE (see figure 6b). Also, 6c image for Ni-SAPO/CPE shows that the nickel ion irregularly aggregated on the surface of fabricated electrode and shows the good adherence of the Ni^{2+} to cavities of SAPO nano molecular sieves and the surface of SAPO/CPE was completely covered with spherical nickel particles [49].

EDX spectroscopy analysis was also taken which provides useful information about the presence of elements and their composition in the structure of electrodes. Figure 6d–f

Figure 6. The representative FESEM images of (a) bare CPE, (b) SAPO/CPE and (c) Ni-SAPO/CPE. The EDX spectra of (d) bare CPE, (e) SAPO/CPE and (f) Ni-SAPO/CPE.

represents the EDX spectra of fabricated CPE, SAPO/CPE and Ni-SAPO/CPE, respectively, and extracted data from these figures are listed in table 1. The obtained data in these figures and table 1 demonstrate that carbon, silicon, aluminum, phosphor and nickel are presented in the composition of the Ni-SAPO/CPE electrode.

The electrochemical behaviour of Ni-SAPO/CPE was considered in 0.1 M NaOH at various scan rates. Figure 7a displays the CVs of the Ni-SAPO/CPE electrode in 0.1 M NaOH at various scan rates. Obviously, the anodic and cathodic currents were enriched with increasing scan rate and a potential shifted to positive values. The positive shift may be due to the ohmic drop, which generated at high current density [50]. The interpretation of observed behaviour is possible according to a theory described by Laviron for the linear potential sweep voltammetric response in the case of surface-confined electroactive species at the small concentrations [51]. The expressions for peak to peak separation of

$\Delta E_p > 0.2 \text{ nV}$ (n = number of exchanged electrons) can be written as the following equations:

$$E_{pa} = E^0 + X \ln \left[\frac{1 - \alpha}{m} \right], \quad (3)$$

$$E_{pc} = E^0 + Y \ln \left[\frac{\alpha}{m} \right], \quad (4)$$

$$\log k_s = \alpha \log (1 - \alpha) + (1 - \alpha) \log \alpha - \log \left(\frac{RT}{nFv} \right) - \left(\frac{\alpha (1 - \alpha) nF \Delta E_p}{2.303 RT} \right), \quad (5)$$

where $X = RT/(1 - \alpha)nF$, $Y = RT/\alpha nF$, $m = (RT/F)(k_s/nv)$, E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. The α , k_s and v are the electron-transfer coefficient, apparent charge-transfer rate constant and scan rate, respectively. From these expressions, α can be obtained by measuring the variation of E_p with respect to the scan rate, and k_s can be calculated for electron transfer between the electrode and the surface-deposited layer by measuring the E_p values. From figure 7b and using equations (3) and (4), the value of anodic electron transfer coefficient (α) is determined as 0.555. It has been suggested that the rate-limiting steps for cathodic and anodic might be the same step [52]. According to the equation (5), the mean value of charge-transfer rate constant (k_s) is found to be 0.022 s^{-1} .

Table 1. Amounts of the elements in the structure of fabricated electrodes.

Electrode	Atomic percentage					
	C	O	Al	Si	P	Ni
CPE	87.1	11.3	0.7	0.9	—	—
SAPO/CPE	60.8	20.1	8.8	2.1	8.2	—
Ni-SAPO/CPE	53.7	19.8	8.5	1.9	7.9	8.2

Figure 7. (a) Cyclic voltammograms recorded for Ni-SAPO/CPE in 0.1 M NaOH at scan rates of 0.005 to 0.3 V s^{-1} , (b) plot of E_p vs. $\log v$ of the cyclic voltammograms for the anodic peaks a and cathodic peaks b , (c) the dependency of I_{pa} and I_{pc} on lower values of v (0.005 – 0.075 V s^{-1}) and (d) the dependency of I_{pa} and I_{pc} on $v^{1/2}$ at higher values of v ($v > 0.075 \text{ V s}^{-1}$).

Figure 7c displays plots of I_{pa} and I_{pc} for oxidation–reduction of the $NiOOH/Ni(OH)_2$ redox couple vs. scan rate at low values from 0.005 to 0.075 $V s^{-1}$. The electrode surface coverage (Γ^*) can be calculated from the linear part of the plot and using the following equation, which correspond to reversible process with adsorbed species [53].

$$I_p = \frac{n^2 F^2 \Gamma^* A v}{4RT}, \quad (6)$$

where I_p , n , Γ^* and A are the peak current, the number of electrons involved in the reaction ($n = 1$), the surface coverage of the redox species and the surface area of the electrode (0.096 cm^2), respectively. The total surface coverage of the immobilized active species is found to be about $5.995 \times 10^{-6} mol cm^{-2}$, considering the mean of both anodic and cathodic currents. Also, the amount of loaded nickel onto the Ni-SAPO/CPE film is about 352.47 $\mu g cm^{-2}$ and the mass of nickel incorporated in the electrode matrix with surface area of 0.096 cm^2 is obtained to be 33.74 μg . At scan rates larger than 0.075 $V s^{-1}$, both the anodic and cathodic peak currents depend on root mean square of scan rate ($v^{1/2}$) that express a diffusion controlled process dominates with increasing scan rates (see figure 7d). This limiting-diffusion process can be related to the charge neutralization of the electrode surface during the oxidation/reduction process [43].

3.4 Electrocatalytic oxidation of methanol onto Ni-SAPO/CPE

Figure 8 shows the electrochemical response of Ni-SAPO/CPE in the absence and presence of 0.003 M methanol in 0.1 M NaOH recorded at a potential sweep rate of 20 $mV s^{-1}$. In the presence of methanol, an increase in current was observed at the surface of Ni-SAPO/CPE (figure 8, curve b) but no significant change in the current intensity was observed at the surface of Ni-CPE (data not shown). These

Figure 8. The cyclic voltammograms of Ni-SAPO/CPE in 0.1 M NaOH at scan rate of 20 $mV s^{-1}$ (a) in the absence of methanol and (b) in the presence of 0.003 M methanol and inset displays Tafel plot derived from the rising part of the cyclic voltammogram shown in b.

figures were revealed that anodic peak current for methanol oxidation is 516 μA , meanwhile anodic current is 313 μA for $Ni(OH)_2/NiOOH$ conversion in the same scan rate (i.e., 20 $mV s^{-1}$) at the surface of Ni-SAPO/CPE. It is observed in figure 8, curve b, that the oxidation of methanol gives rise to a typical electrocatalytic response, with an increase in the anodic peak current and a decrease in the cathodic peak current. The oxidation potential of methanol is detected at ca. 0.66 V that is positive than the potential observed for Ni^{2+} to Ni^{3+} transition at the surface of Ni-SAPO/CPE in the absence of methanol (i.e., 0.6 V). This matter suggests an interaction between the methanol and the redox sites of modified electrode surface and this behaviour is a typical observation expected from the mediated oxidation (EC' mechanism), illustrated in the following equations [11,13,20,26]:

The modified Ni-SAPO/CPE electrode showed electrochemical behaviour that can be explained on the basis of the electrochemical behaviour of smooth nickel electrodes. In alkaline solution reaction, $Ni(OH)_2/NiOOH$ transformation was observed at the potentials close to 0.6 V vs. $Ag|AgCl|KCl$ (3 M) electrode, while at potentials higher than 0.75 V, oxygen evolution occurred evolving from hydroxide ion oxidation [13]. $NiOOH$ formed at Ni-SAPO/CPE with higher Ni content was mixture of β - and γ - $NiOOH$ forms. In the alkaline solution, α - $Ni(OH)_2$ and β - $Ni(OH)_2$ are oxidized into γ - $NiOOH$ and β - $NiOOH$, respectively. Although, α - $Ni(OH)_2$ is very unstable and is easily changed into β - $Ni(OH)_2$ in the alkaline media [10,13]. The SAPO molecular sieves framework stabilized β - $Ni(OH)_2$, which resulted in formation of β - $NiOOH$. Consequently, β - $NiOOH$ is preferred oxide type for methanol oxidation in comparison with γ - $NiOOH$ oxide type [10].

It is commonly established that the Ni-based catalysts such as nickel oxides and its complexes in a basic aqueous medium can catalyse methanol oxidation through an overall four electron processes for producing formate anion according to the following reaction [54]:

To obtain information about the rate determining step, a Tafel plot was depicted for Ni-SAPO/CPE in the presence of 0.003 M CH_3OH at scan rate of 20 $mV s^{-1}$ in 0.1 M NaOH solution. Inset in figure 8 shows the plot of $\log I_p$ vs. E_p using the data derived from the rising part of the current–voltage of curve 8b. The slope of the Tafel plot is equal to $n(1-\alpha)F/2.303 RT$ which comes up to 13.463 V per decade. We obtained α as 0.80.

The electrocatalytic behaviours of the modified electrodes with SAPO molecular sieve ratio of 10, 15, 20, 25 and

30 wt.% with respect to the graphite powder were studied by CV technique in 0.002 M CH₃OH at 0.1 M NaOH solution (see figure 9). It was determined that higher anodic current of methanol oxidation is observed when 25% of SAPO molecular sieve with respect to the graphite powder was used. It is suggested that with increasing the SAPO over than 25% in the modified electrode, the resistance of electrode may increase due to low conductivity of SAPO molecular sieve and a decrease in methanol oxidation current is observed. Also, at lower ratios of SAPO in Ni-SAPO/CPE, the amount of available pores for Ni²⁺ insertion decreases and available NiOOH active site is reduced for methanol oxidation

Figure 9. Histograms of anodic peak currents for Ni-CPE, Ni-SAPO (10%)/CPE, Ni-SAPO (15%)/CPE, Ni-SAPO (20%)/CPE, Ni-SAPO(25%)/CPE and Ni-SAPO (30%)/CPE in the solution containing 0.002 M methanol plus 0.1 M NaOH at a scan rate of 20 mV s⁻¹.

and ultimately cause to low current density [20,31,55]. The amount of 25% (w/w) SAPO with respect to the graphite powder was selected as an optimum value for fabrication of modified electrode in the following experiment.

The effects of various concentrations of methanol were investigated on the voltammetric response of Ni-SAPO/CPE at the scan rate of 20 mV s⁻¹. Increase in the concentration of methanol was followed by an increase in the anodic peak current and decrease in the cathodic peak current up to the concentration of 0.1 M. In the concentrations of more than 0.1 M, no remarkable increase in the anodic peak current was observed (data not shown). It can be specified that this effect may be due to the saturation of active sites and/or poisoning the electrode surface with adsorbed intermediates. Thus, 0.1 M of methanol represented the optimum concentration after which the adsorption of the oxidation products at the electrode surface may cause the stoppage of further oxidation.

The CVs of Ni-SAPO/CPE were investigated in the presence of 0.003 M methanol in 0.1 M NaOH at scan rates between 5 and 500 mV s⁻¹. By an increase in the scan rate, the anodic peak currents (I_{pa}) were increased and the anodic peak potentials shifted to more positive directions. It can be proposed that this shift might be due to ohmic drop [29]. The increase in the peak current with the scan rate can be considered as an adsorption or diffusion control of the process. Figure 10a illustrates the plot of I_{pa} vs. square root of scan rate ($v^{1/2}$), meanwhile figure 10b shows plot of I_{pa} vs. scan rate (v) obtained from CVs of Ni-SAPO/CPE in 0.003 M methanol in 0.1 M NaOH at various scan rates. A plot of I_{pa} vs. the v did not show a linear curve (see figure 10b) meanwhile, a plot of I_{pa} vs. the $v^{1/2}$ was found to be linear with equation of $I_{pa} (\mu A) = 44.556 v^{1/2} (mV s^{-1})^{1/2} + 207.07$

Figure 10. The plots of (a) I_{pa} vs. $v^{0.5}$; (b) I_{pa} vs. v ; (c) $\log I_{pa}$ vs. $\log v$; (d) $I_{pa}/v^{0.5}$ vs. $\log v$ for oxidation of 0.003 M methanol in 0.1 M NaOH at various scan rates in the surface of Ni-SAPO/CPE.

and $R^2 = 0.9804$ (see figure 10a). This observation indicated that this process is diffusion-controlled process rather than surface-controlled process. Also, figure 10a indicates that the oxidation current for methanol increased linearly with the square root of the scan rate, indicating that the reaction is mass transfer controlled [53].

From theoretical point, a slope of 0.5 or 1 is expected for the plot of $\log I_{pa}$ vs. $\log \nu$ under diffusion or adsorption control, respectively [11]. A linear dependence is detected between $\log I_{pa}$ vs. $\log \nu$ at the surface of Ni-SAPO/CPE in the oxidation of methanol (see figure 10c). The slope of 0.3396 is obtained from linear section of curve that is near to the theoretically predicted value of 0.5 for a purely diffusion controlled process. However, the contribution of a kinetic limitation to the overall process cause a small alteration with theoretical value [56]. By considering the plot of scan rate normalized current ($I_{pa}/\nu^{0.5}$) vs. $\log \nu$ (see figure 10d), the characteristic shape of an EC' process is observed which expresses that the electrode reaction is coupled with an irreversible follow up chemical step [43,57]. Also at higher potential scan rates, the cathodic peak current relating to Ni(III) reduction to Ni(II) appears which confirms EC' mechanism [50].

3.5 Chronoamperometric studies

Chronoamperometry technique gets more information about electrooxidation of methanol and evaluate the electrocatalytic performance, catalytic rate constant of methanol oxidation on the surface of modified electrodes. Figure 11a shows

the double-step chronoamperograms ($I-t$ curves) of redox process at the surface of the Ni-SAPO/CPE with several concentrations of methanol (i.e., 0.0, 0.0015, 0.003, 0.004, 0.005, 0.0075 M). The applied potential steps were 0.78 and 0.31 V vs. Ag|AgCl|KCl (3 M) in the anodic and cathodic directions, respectively. The forward and backward potential steps of chronoamperometry of the Ni-SAPO/CPE electrode in the blank solution showed an almost symmetrical chronoamperogram, which displays that almost equivalent charges were consumed for the oxidation and reduction of surface-confined Ni(OH)₂/NiOOH sites. However, in the presence of methanol, the charge value associated with the forward chronoamperometry is greater than that observed for the backward chronoamperometry (see figure 11b).

We can calculate the value of catalytic rate constant (k_{cat}) of the electrooxidation of methanol on the active sites of the Ni-SAPO/CPE according to the following equation [58].

$$\frac{I_{cat}}{I_L} = \pi^{1/2} (k_{cat} c_0 t)^{1/2}, \quad (7)$$

where I_{cat} and I_L are the currents in the presence and absence of methanol, respectively. The symbol k_{cat} is the catalytic rate constant ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$), c_0 the bulk concentration of methanol (mol cm^{-3}) and t the elapsed time (s). Figure 11c shows the plot of I_{cat}/I_L vs. $t^{1/2}$ derived from the data of chronoamperograms in the absence and presence of 0.005 M methanol. From the slopes of the I_{cat}/I_L vs. $t^{1/2}$ for all concentrations, the mean value of k_{cat} was calculated to be $4.62 \times 10^4 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$. Comparison of the estimated k_{cat}

Figure 11. (a) The double-step chronoamperogram obtained from Ni-SAPO/CPE *a* in the absence and presence of *b* 0.0015, *c* 0.003, *d* 0.004, *e* 0.005 and *f* 0.0075 M methanol in 0.1 M NaOH solution. First and second potential steps were 0.78 and 0.31 V vs. Ag|AgCl|KCl (3 M), respectively. (b) Charge–time curves *a* in the absence and *b* presence of 0.004 M methanol. (c) Dependence of I_{cat}/I_L on $t^{1/2}$, derived from the data of chronoamperograms in the absence and presence of 0.005 M methanol. (d) Dependence of I on $t^{-1/2}$, derived from the data of chronoamperogram in the presence of 0.005 M of methanol. (e) Dependence between slope of curve *d* vs. methanol concentration.

with other catalytic rate constant values in the literature is performed and presented in table 2.

An exponential behaviour of $I-t$ curves displays that a diffusion-controlled process has occurred according to Cottrell equation. From the chronoamperometric investigation, the diffusion coefficient of methanol (D) was determined in aqueous solution by Cottrell equation [12,59]:

$$I = nFACD^{1/2} \cdot \pi^{-1/2} \cdot t^{-1/2}, \quad (8)$$

where n is the number of electron (i.e., 4) [42], F is the Faraday number (96485 C mol^{-1}), A the area of the electrode (0.096 cm^2), C the known concentration of methanol and D is the apparent diffusion coefficient. Figure 11d displays experimental plots of I vs. $t^{-1/2}$ for 0.005 M of methanol at the surface of Ni-SAPO/CPE. The similar curves were plotted for all concentrations and then the slopes of the resulting straight lines were plotted vs. the methanol concentration (see figure 11e). From the slope of the resulting plot and

using equation (8), the mean value of the D was found to be $1.16 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Performance of the proposed electrode was investigated by a comparison between Ni-SAPO/CPE and some of the previously reported modified electrodes for electrocatalytic oxidation of methanol. Table 3 exhibits the peak potential and peak current density of methanol electrooxidation on Ni-SAPO/CPE and a comparison with some of the previously reported modified electrodes in the literature. By comparing the values in table 3, it can be deduced that Ni-SAPO/CPE has good catalytic performance in the oxidation of methanol and is a good candidate for further investigation.

3.6 Reproducibility and stability of the Ni-SAPO/CPE

The reproducibility and stability of the Ni-SAPO/CPE were evaluated by comparing of the currents of different electrodes using CV technique (see figure 12). The anodic current of the

Table 2. Comparison of the catalytic rate constant of Ni-SAPO/CPE for electrocatalytic oxidation of methanol with some of the previously reported electrodes in 0.1 M NaOH.

Electrode	Modifier	$k_{\text{cat}} (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	Ref.
Ni-SBA-15/CPE	Ni(OH) ₂	1.10×10^4	[31]
Ni-SBA-16/CPE	Ni(OH) ₂	1.184×10^3	[32]
MWCNTPE	Ni(II)-quercetin	1.83×10^6	[60]
Carbon nanotube paste	N/POT (TX-100)	7.4×10^4	[61]
Ni-ZSM-5/CPE	Ni(OH) ₂	3.3×10^4	[62]
Ni-NZM/CPE	Ni(OH) ₂	2.54×10^4	[63]
Poly-Ni(II)-curcumin/GC	Ni(II)-curcumin	2.04×10^3	[64]
Ni-NiY/CPE	Ni(OH) ₂	1.56×10^4	[65]
Ni-POAP/CPE	Ni(OH) ₂	86.7	[66]
Ni-SAPO/CPE	Ni(OH) ₂	4.62×10^4	This work

Table 3. Comparison of the oxidation potential and current density (J) of some nickel modified electrodes applied in the electrocatalytic oxidation of methanol in alkaline medium.

Electrode	Scan rate (mV s^{-1})	E_p/V vs. Ag/AgCl	Current density (mA cm^{-2}) ^a	Ref.
Ni-VSB-5/CPE	20	0.92	7.4	[20]
Ni-ZSM/CPE	20	0.72	9.2	[29]
Ni-SBA-15/CPE	25	0.80	14.2	[31]
Ni-SBA-16/CPE	25	0.76	16.63	[32]
Ni-ANA/CPE	20	0.75	9.0	[33]
Ni-NZM/CPE	50	0.83	8.3	[55]
Ni/POT (TX-100)/CPE	20	0.70	18.5	[61]
Poly-Ni(II)-curcumin/GC	100	0.77	17.2	[64]
Ni-NiY/CPE	20	0.78	5.5	[65]
Ni/POAP/CPE	20	0.70	3.7	[66]
Ni/NiDMG	20	0.64	15.9	[67]
Ni(OH) ₂ /GC	50	0.58	15.4	[68]
Poly-(Ni ^{II} -tmdbta)/GC	100	0.61	1.5	[69]
Ni-SAPO/CPE	20	0.66	5.36	This work

^a $J = I_p/A$ (A = geometric surface area of substrate).

Figure 12. Variation of electrocatalytic currents of five Ni-SAPO/CPE electrodes for oxidation of 0.003 M methanol in 0.1 M NaOH solution. Error bars represent standard deviation.

five modified Ni-SAPO/CPE electrodes to electrocatalytic oxidation of 0.003 M methanol in 0.1 M NaOH solution was experienced independently, and the relative standard deviation (RSD) was obtained to be 4.3%. A reproducible current response with a RSD of 3.5% was observed for 5 successive assays of 0.003 M methanol in 0.1 M NaOH solution by one modified electrode. The long-term stability was explored by measuring a methanol solution intermittently, and the electrode was stored at room temperature when it is not in use. After 1 and 3 months, the Ni-SAPO/CPE electrode response to electrocatalytic oxidation of methanol retains 93 and 87% of the initial value, respectively.

4. Conclusions

In summary, a method was reported for the synthesis of nano-sized silicoaluminophosphate molecular sieves. Result from SEM image and XRD pattern demonstrate that the synthesized SAPO molecular sieve is a semispherical particle with a size of 26.75 nm. A novel modified CPE was developed by this molecular sieve. This new modified electrode (Ni-SAPO/CPE) was utilized towards the electrocatalytic oxidation of methanol in alkaline solution, and the results were examined by cyclic voltammetry and chronoamperometry techniques. The CVs showed that Ni-SAPO/CPE increased the oxidation current of methanol as compared to Ni-CPE. The porous structure and large surface area of SAPO molecular sieves make a framework for Ni^{2+} uptake, which is converted to $\text{Ni}(\text{OH})_2$ and NiOOH during the anodic oxidation in alkaline solution. In the alkaline solution, $\alpha\text{-Ni}(\text{OH})_2$ and $\beta\text{-Ni}(\text{OH})_2$ are oxidized into $\gamma\text{-NiOOH}$ and $\beta\text{-NiOOH}$, respectively. Although, $\alpha\text{-Ni}(\text{OH})_2$ is very unstable and is easily changed into $\beta\text{-Ni}(\text{OH})_2$ in the alkaline media. Also, the SAPO molecular sieves framework stabilized $\beta\text{-Ni}(\text{OH})_2$ which resulted in formation of $\beta\text{-NiOOH}$ and this species is preferred oxide type for methanol oxidation in comparison to $\gamma\text{-NiOOH}$ oxide type. Results specified that the modified

electrode decreased the overpotential of the methanol oxidation and increased the kinetics of reaction by a catalytic process in alkaline medium. Also, the NiOOH species formed during the oxidation of Ni-SAPO/CPE is found to be a good catalyst for oxidation of methanol. The ease and fast preparation and obtaining a new reproducible surface, the low residual current, porous surface, low cost and stability, stable response and very low ohmic resistance in fuel cell are some advantages of Ni-SAPO/CPE.

References

- [1] Parsons R and Vandernoot T 1988 *J. Electroanal. Chem.* **257** 9
- [2] Nishimura K, Machida K and Enyo M 1988 *J. Electroanal. Chem.* **251** 117
- [3] Lima A, Coutanceau C, Leger J M and Lamy C 2001 *J. Appl. Electrochem.* **31** 379
- [4] Abdel Rahim M A, Abdel Hameed R M and Khalil M W 2004 *J. Power Sources* **134** 160
- [5] Raoof J B, Karimi M A, Hosseini S R and Mangelizadeh S 2010 *J. Electroanal. Chem.* **638** 33
- [6] Rahimnejad M, Hassaninejad-Darzi S K and Pourali S M 2015 *J. Iran. Chem. Soc.* **12** 413
- [7] Ourari A, Nora H, Noureddine C and Djouhra A 2015 *Electrochim. Acta* **170** 311
- [8] Adams R N 1958 *Anal. Chem.* **30** 1576
- [9] Ojani R, Raoof J B and Khanghah Y A 2011 *Electrochim. Acta* **56** 3380
- [10] Mojovic Z, Bankovic P, Jovic-Jovicic N, Milutinovic-Nikolic A, Abu Rabi-Stankovic A and Jovanovi D 2011 *Int. J. Hydrogen Energy* **36** 13343
- [11] Fleischmann M, Korinek K and Pletcher D 1971 *J. Electroanal. Chem.* **31** 39
- [12] Taraszewska J and Rosłonek G 1994 *J. Electroanal. Chem.* **364** 209
- [13] Danaee I, Jafarian M, Forouzandeh F, Gopal F and Mahjani M G 2008 *Int. J. Hydrogen Energy* **33** 4367
- [14] Abdel Rahim M A, Hassan H B and Abdel Hamid R M 2006 *J. Power Sources* **154** 59
- [15] Danaee I, Jafarian M, Forouzandeh F, Gopal F and Mahjani M G 2009 *Int. J. Hydrogen Energy* **34** 859
- [16] Bidault F, Brett D J L, Middleton P H, Abson N and Brandon N P 2009 *Int. J. Hydrogen Energy* **34** 6799
- [17] Habibi B and Gahramanzadeh R 2011 *Int. J. Hydrogen Energy* **36** 1913
- [18] Sun L, Hao Y, Zhang C, Ran R and Shao Z 2010 *Int. J. Hydrogen Energy* **35** 7971
- [19] Breck D W 1974 *Zeolite molecular sieves: structure, chemistry and use* (New York: Wiley)
- [20] Samadi-Maybodi A, Hassani Nejad-Darzi S K, Ganjali M R and Ilkhani H 2013 *J. Solid State Electrochem.* **17** 2043
- [21] Tanaka K, Choo C K, Sumi S, Kamitani Y, Fujii T, Satoh K et al 2002 *J. Phys. Chem. B* **106** 4155
- [22] Hudson M R, Queen W L, Mason J A, Fickel D W, Lobo R F and Brown C M 2012 *J. Am. Chem. Soc.* **134** 1970

- [23] Pires J, Fernandes A C and Duraiswami D 2014 *Chin. J. Catal.* **35** 1492
- [24] Nishanth K G, Sridhar P, Pitchumani S and Shukla A K 2013 *Bull. Mater. Sci.* **36** 353
- [25] Aghaei E and Haghighi M 2015 *Powder Technol.* **269** 358
- [26] Raoof J B, Chekin F and Ehsani V 2015 *Bull. Mater. Sci.* **38** 135
- [27] Tonscheidt A, Ryder P L, Jaeger N I and Schulz-Ekloff G 1996 *Zeolites* **16** 271
- [28] Mentus S, Mojovic Z, Cvjeticanin N and Tesic Z 2004 *J. New Mater. Electrochem. Syst.* **7** 213
- [29] Raoof J B, Azizi N, Ojani R, Ghodrati S, Abrishamkar M and Chekin F 2011 *Int. J. Hydrogen Energy* **36** 13295
- [30] Abrishamkar M, Azizi S N and Raoof J B 2012 *Monatsh. Chem.* **143** 409
- [31] Azizi S N, Ghasemi S and Chiani E 2013 *Electrochim. Acta* **88** 463
- [32] Azizi S N, Ghasemi S and Yazdani-Sheldarrei H 2013 *Int. J. Hydrogen Energy* **38** 12774
- [33] Azizi S N, Ghasemi S and Gilani N S 2014 *Chin. J. Catal.* **35** 383
- [34] Yang J, Tan J, Yang F, Li X, Liu X and Ma D 2012 *Electrochem. Commun.* **23** 13
- [35] Lin S, Li J, Sharma R P, Yu J and Xu R 2010 *Top. Catal.* **53** 1304
- [36] Yang G, Wei Y, Xu S, Chen J, Li J, Liu Z, Yu J and Xu R 2013 *J. Phys. Chem. C* **117** 8214
- [37] Izadbakhsh A, Farhadi F, Khorasheh F, Sahebdehfar S, Asadi M and Feng Y Z 2009 *Appl. Catal. A—Gen.* **364** 48
- [38] Treacy M M J and Higgins J B 2007 *Collection of simulated XRD powder patterns for zeolites*, 5th revised edn, Published on behalf of the Structure Commission of the International Zeolite Association (Amsterdam, Jordan Hill: Elsevier)
- [39] Sang S, Chang F, Liu Z, He C, He Y and Xu L 2004 *Catal. Today* **93–95** 729
- [40] Klug H P and Alexander L E 1964 *X-ray diffraction procedures*, 2nd edn (New York: Wiley)
- [41] Liu G, Tian P, Li J, Zhang D, Zhou F and Liu Z 2008 *Micropor. Mesopor. Mater.* **111** 143
- [42] Beitollah H, Goodarzi M, Khalilzadeh M A, Karimi-Maleh H, Hassanzadeh M and Tajbakhsh M 2012 *J. Mol. Liq.* **173** 137
- [43] Hassaninejad-Darzi S K 2014 *J. Electroceram.* **33** 252
- [44] Gharibi H, Kakaei K and Zhiani M 2010 *J. Phys. Chem. C* **114** 5233
- [45] El-Shafei A A, Elhafeez A M A and Mostafa H A 2010 *J. Solid State Electrochem.* **14** 185
- [46] Nagashree K L and Ahmed M F 2010 *J. Solid State Electrochem.* **14** 2307
- [47] Bode H, Dehmelt K and Witte J 1966 *Electrochim. Acta* **11** 1079
- [48] Mojovic Z, Mentus S and Krstic I 2007 *Russ. J. Phys. Chem. A* **81** 1452
- [49] Ojani R, Raoof J B and Safshekan S 2012 *J. Appl. Electrochem.* **42** 81
- [50] Ojani R, Raoof J B and Zamani S 2012 *Bioelectrochemistry* **85** 44
- [51] Laviron E 1979 *J. Electroanal. Chem.* **101** 19
- [52] Luo H, Shi Z, Li N, Gu Z and Zhuang Q 2001 *Anal. Chem.* **73** 915
- [53] Bard A J and Faulkner L R 2001 *Electrochemical methods: fundamentals and applications* (New York: Wiley)
- [54] Cardoso W S, Dias V L N, Costa W M, Rodrigues I A, Marques E P, Sousa A G et al 2009 *J. Appl. Electrochem.* **39** 55
- [55] Hassaninejad-Darzi S K and Rahimnejad M 2014 *J. Iran. Chem. Soc.* **11** 1047
- [56] Velazquez-Palenzuela A, Centellas F, Garrido J A, Arias C, Rodriguez R M, Brillas E and Cabot P L 2011 *J. Power Sources* **196** 3503
- [57] Gosser D K 1994 *Cyclic voltammetry simulation and analysis of reaction mechanism* (New York: Wiley)
- [58] Galus Z 1976 *Fundamentals of electrochemical analysis* (New York: Ellis Horwood)
- [59] Greef R, Peat R, Peter L M, Pletcher D and Robinson J 1990 *Instrumental methods in electrochemistry* (Chichester: Ellis Horwood)
- [60] Xue T, Wang Y M and He M Y 2012 *Micropor. Mesopor. Mater.* **156** 29
- [61] Raoof J B, Ojani R and Hosseini S R 2011 *J. Power Sources* **196** 1855
- [62] Ojani R, Raoof J B and Salmany-Afagh P 2004 *J. Electroanal. Chem.* **571** 1
- [63] Fontana M G 1987 *Corrosion engineering* (New York: McGraw-Hill)
- [64] Ciszewski A, Milczarek G, Lewandowska B and Krutowski K 2003 *Electroanalysis* **15** 518
- [65] Ojani R, Raoof J B, Fathi S and Alami-Valikchali S 2011 *J. Solid State Electrochem.* **15** 1935
- [66] Ojani R, Raoof J B and Fathi S 2009 *J. Solid State Electrochem.* **13** 927
- [67] Golikand A N, Asgari M, Maragheh M G and Shahrokhian S 2006 *J. Electroanal. Chem.* **588** 155
- [68] El-shafei A A 1999 *J. Electroanal. Chem.* **471** 89
- [69] Liu S J 2004 *Electrochim. Acta* **49** 3235