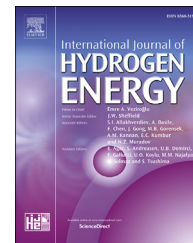




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Fe³⁺-Clinoptilolite/graphene oxide and layered MoS₂@Nitrogen doped graphene as novel graphene based nanocomposites for DMFC

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ABSTRACT

Fe³⁺ doped in a natural zeolite (Fe³⁺-Clinoptilolite) hybridized with graphene oxide (GO) was used as an electro-catalyst for methanol oxidation in direct methanol fuel cells (DMFC). Furthermore, thin layered molybdenum disulfide (MoS₂) composited with nitrogen doped graphene (NG) was used for oxygen reduction. Successful synthesis of these nano-materials was confirmed by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FTIR), energy-dispersive X-ray (EDX), Raman spectroscopy, Field Emission Scanning Electron Microscopy (FESEM) and transmission electron microscopy (TEM) images. In the following, by using the cyclic voltammetry (CV) technique the electrochemical behaviors of the glassy carbon electrodes modified with the mentioned composites were investigated. The results of methanol oxidation and oxygen reduction showed sufficient electro-catalytic effects as well as significant diffusion currents in presence of the non-precious synthetic materials. Obtained exchange currents (*i*₀) from Tafel plots showed increasment up to 6.02×10^{-6} and 1.47×10^{-5} μA for anode and cathode respectively. Also, thermodynamic potential of the DMFC was estimated about 1.1 V in alkaline media that was very close to reported value for theoretical potential in DMFC.

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Introduction

Nowadays with regard to the energy crisis restriction of fossil fuels and pollution originated from them, the use of new energy producers has been noticed more than before. Accordingly, fuel cells are one of researchers' efforts to overcome these challenges [1]. Various fuels are being used in fuel cells such as hydrocarbons, alcohols etc [2]. However among the alcohols, methanol seems to be more appropriate because of

simplicity and possessing few carbon atoms [3]. But low current density of methanol related to hydrogen fuel requires precious metallic catalysts like platinum and its alloys [4], palladium [5], gold [6], etc.

Zeolites have many applications as catalyst [7] adsorbent [8] and separator [9]. These inorganic materials with crystalline three dimensional structures of tetrahedral SiO₄ and AlO₄ possess abundant channels and suitable space for deployment of various chemical species [10]. This kind of structure

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leads to extra negative charges on the surface of zeolite particles that can be neutralized by cations [11]. Clinoptilolite is a naturally accessible and plentiful type of zeolite with unit cell formula: $[\text{Na}_{0.1}\text{K}_{8.57}\text{Ba}_{0.04}(\text{Al}_{9.31}\text{Si}_{26.83}\text{O}_{72}) \cdot 19.56\text{H}_2\text{O}]$ and great cation exchange capacity [12,13]. Considering high Si:Al ratio of Clinoptilolite, it is expected that forming the extra-zeolite species is trivial so the electroactive reactants penetration and subsequently the catalyst performance will be improved [14]. On the other hand, impermeability of Clinoptilolite for methanol molecules in terms of crossover is very fascinating [15].

Graphene is a nanomaterial of monolayer or multilayer of carbon atoms in a beehive-shaped structure that are compressed together [16]. Unique properties for graphene in nanoelectronic industries [17], energy storage [18–21], sensors [22] etc are reported. Doping of heteroatoms like nitrogen having lone pair nonbonding electrons can cause delocalizing SP^2 hybridization system that leads to improving electrocatalytic activities of graphene [23]. That would be reasonable for change of asymmetric spin density and charge density which leads to enhancement of electrocatalytic effect for oxygen reduction reactions (ORR) [24].

Molybdenum disulphide, MoS_2 as a metal chalcogenide, is a layered polycrystalline nano material having properties such as large surface area and electrocatalytic active sites [25,26] that have been used in hydrogen production [27,28], capacitive deionization [29] and storage devices [30,31]. The surface of MoS_2 nanosheets increases contact area and consequently improve electrocatalytic effects of this nanomaterial [32]. One of the disadvantages of MoS_2 is its weak conductivity, so hybridizing it with graphene or its derivatives can resolve this problem as well as giving the role of a new electro-catalyst for oxygen reduction reaction [33]. MoS_2 and nitrogen doped graphene (NG) can be accumulated via $\pi - \pi$ interactions of MoS_2 layers with graphene nano sheets. On the other hand, the formation of this hybrid enhances MoS_2 electrical conductivity and lowers resistance against electron transfer for reactant through activating catalytic sites of MoS_2 [34–38].

Electrocatalytic oxidation of methanol has been widely studied, including methanol oxidation on cupreous palladium decorated composite [39], platinum–tungsten trioxide as double component nanocomposite [40], and ruthenium–platinum core–shell nanocatalyst [41]. Despite good results in methanol oxidation, expensive materials used in structure of these nanocomposites are a burning problem.

In the current study, Fe^{3+} -Clinoptilolite as a mineral and inexpensive material and MoS_2 with a simple synthetic procedure along with graphene derivatives were prepared to increasing a DMFC performance. Successful nanocomposites synthesis was confirmed by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FT-IR), Field Emission Scanning Electron Microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray (EDX) and Raman spectroscopy techniques. Electrocatalytic properties of the nanocomposites were studied by modification of the glassy carbon electrode (GCE) by the prepared materials. Using Fe^{3+} -Clinoptilolite/graphene oxide as anode and MoS_2 @NG as cathode materials, we have obtained significant promising results for designing an inexpensive and efficient direct methanol fuel cell with evidences

from the Tafel plots. Along with the results, it was showed the electroactivity for methanol oxidation is highly dependent on presence of Fe^{3+} in the zeolite structure through an extra zeolitic mechanism. On the other hand MoS_2 @NG with nanosheet structure showed electrocatalytic properties for oxygen reduction with shifting the reduction potential to more positive values (decreasing overvoltage) and enhancement in cathodic peak current.

Experimental

Chemicals and instrumentals

Natural Clinoptilolite zeolite was prepared from tuffs in Semnan region, Iran. The solution of Nafion 117 (5%) in mixture of water and low chain aliphatic alcohols was purchased from Aldrich. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and Graphite powder were prepared from Merck. Melamine powder (1,3,5 Triazine-2,4,6-Triamine) and L-cysteine were purchased from Acros. Other used chemicals were prepared in analytical grade from Merck. Electrochemical studies were performed by Autolab P/GSTAT 12 electrochemical system, the Netherlands, with the related standard glassy carbon as working, Ag/AgCl (3 M KCl) as reference and Pt rod as counter electrodes.

Synthesis of Fe^{3+} -Clinoptilolite

For preparation of Fe^{3+} doped Clinoptilolite, after washing the zeolite powder with double distilled water in order to removing soluble impurities, 0.2 g of dried zeolite was dispersed in 40 ml of Fe^{3+} (0.5 M from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). Then the diluted solution of HNO_3 was added (for maintenance of iron ions in triple positive charge) and stirred magnetically in room temperature for 24 h. After that, the acquired suspension was centrifuged in 5000 rpm for 1 h. The precipitate was washed with double distilled water for two times and with diluted HNO_3 for one time and then dried in 100 °C oven for 24 h. In order to show the crystalline structure of the prepared Fe^{3+} -Clinoptilolite and compare it with pristine Clinoptilolite, X-ray diffraction (XRD) spectra were prepared. To make sure the existence of iron in zeolite samples, X-ray fluorescence (XRF) spectra were also obtained.

Synthesis of nitrogen doped graphene (NG)

In a typical procedure, graphene oxide (GO) was prepared based on Hummers' method using graphite powder [42]. In order to prepare NG, 1:5 mass ratio of GO and the melamine powder (1,3,5 Triazine-2,4,6-Triamine) were mixed and introduced to ceramic crucible, heated in furnace equipped with argon flow up to 800 °C for one hour with 5° per minute rate, and then cooled in room temperature. An FTIR spectrum was prepared from the dark brown product in order to show nitrogen in graphene structure.

Synthesis of MoS_2 @NG and MoS_2 @GO nano-layers

MoS_2 @NG and MoS_2 @GO nanolayers were prepared from a method based on a previous report [43]. Briefly, synthesized

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