

Obtaining a Hybrid Electrode Based on Imidazonium Ion- terminated and Metallic Nano-Clusters for Battery Electrode Use

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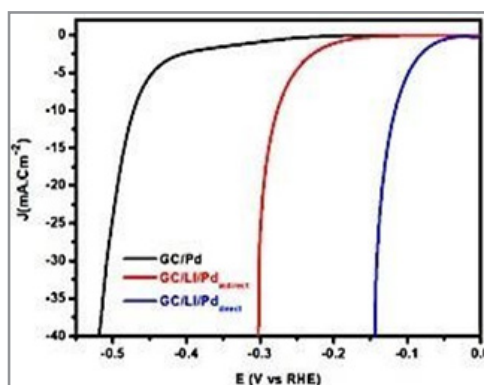
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Abstract

Surface modification with thin organic layers is crucial for designing materials with specific properties to develop practical applications such as supercapacitors, metal-air batteries; fuel cells, corrosion resistance. In the present work, we focused on the grafting of thin film positively charged; i.e. ionic liquids (LIs) on a glassy carbon electrode (GC), then functionalized with metal nanoparticles (Pt or Pd). The SEM obtained images confirm the modified electrode. Then its catalytic performances towards the hydrogen evolution reaction (HER) were evaluated. Interestingly, the catalytic performances are improved for both prepared electrodes (GC/LI/Pt, GC/LI/Pd), especially the latest one containing palladium. It seems that the ionic layer presence displays an increase catalytic, which is probably due to the synergistic effect existence between the grafted ionic layer and the metallic nanoparticles.



Keywords: Ionic Liquid, Nanoparticles, Modified Electrode, Electrocatalysis, Hydrogen Evolution Reaction

Topic 2: Organic and inorganic formulations and synthesis: inhibitors, catalysts and chemical products.

Introduction

Surface chemistry offers an interesting approach to modulate the materials properties. So, several approaches were described leading to the anchoring various functional molecules onto different materials [1]. The electrochemical approaches are re-

ported to be an efficient process for obtaining an immobilized thin organic layer, having few nanometers thick deposited on different electrode material (metals, carbon, semiconductor and nanomaterials) [2]. Among the electrochemical methods the diazonium derivatives reduction is the most used and attractive

approach, in which we are interested. So as diazonium, we have chosen à LI, because these compounds become very attractive in the scientific and industrial fields, due to their interesting physicochemical properties [3-5]. Indeed, several reported works highlight the immobilized LIs potential applications, onto different supports, in energy storage and conversion, and smart materials [6, 7]. Different substrates were used and we choose, to use the glassy carbon (GC) [8, 9]. Because, this inert material displays a weak activity towards the small molecules electrochemical activation including HER, which make it a material of choice as a support electrode.

Post-functionalization is complementary functionalization leading to enhance surface modification and to decorate the previously modified electrode surface. For this purpose, several strategies were reported including chemical surface reaction, i.e. peptide coupling, Gomberg-Bachmann coupling and click

chemistry, and electrochemical deposition [10-12]. In this work, the GC was initially modified by electrografting of LI (1-nitrophenylethyl 3-methylimidazolium bis (trifluoromethyl- sulfonyl)imide, [NO₂-phenyl- Im] [TFSI]), according to the previously reported procedure. Then the GC/LI electrode was used as working electrode, for further functionalization with platinum or palladium electrochemical deposited. So, this modified electrode was immersed in aqueous electrolytic solution containing 10-3 mol/L of K₂PtCl₄ or Na₂PdCl₄, then a chronoamperometry was performed, by applying negative potentials of -0.4 V/Ag/AgCl, to produce the GC/LI/Pt and GC/LI/Pd.

Results

The SEM

The SEM image reported in Fig. 1 was performed on GC/Pt and GC/LI/Pt samples displays many bright spots indicating metallic platinum presence.

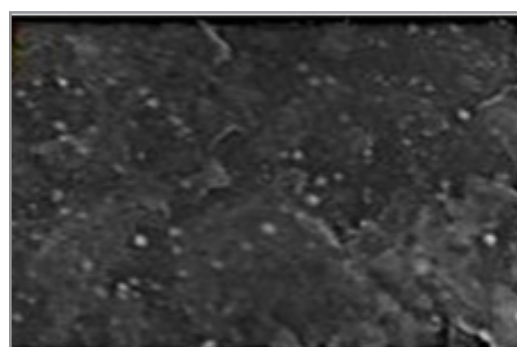
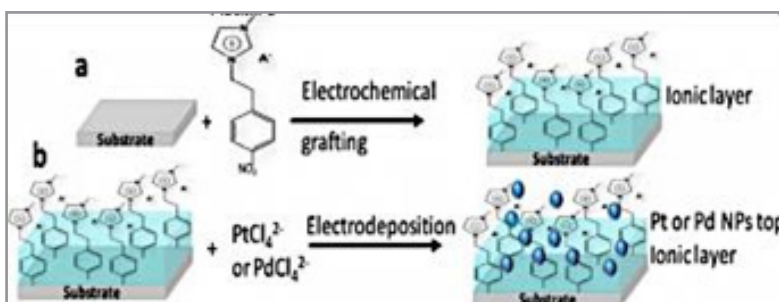


Figure 1: Modified Electrode SEM Image of the GC/Pt (a), GC/LI/Pt (b)

In addition, the image shows a homogeneous nanoparticles distribution onto the GC/LI modified electrode with an average size around 10 nm (Fig1-b). While, for electrode without ionic layer, the GC/Pt SEM images display less homogeneous particles dis-

tribution and higher particles size (around 50 nm) (Fig1-a). This result indicates LI electrodeposition and metal nanoparticles formation into the organic layer as shown in the schema 1.



Schema 1: (a) Electrochemical Grafting of the LI. (b) Electrochemical Deposition of Pt or Pd on GC/LI

Furthermore, the electrochemical and morphological observations suggest a difference on the metal NP's nucleation growth process during its deposition on GC compared to GC/LI substrate.

Electrochemical Investigations of HER Activity

The Pt or Pd electrochemical deposition onto GC/LI was performed by chronoamperometry at a potential - 0.4 V vs Ag/AgCl. Then the electrocatalytic performances of the generated GC/LI/metal NP towards the HER were investigated.

Platinum

In the Pt case, the HER Polarization Curve and Corresponding Tafel Plots are Performed and Reported in Fig.2 a.

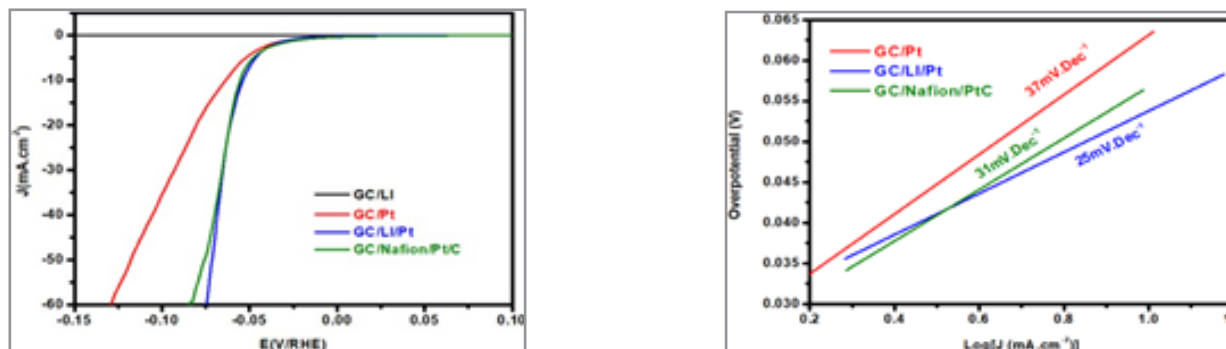


Figure. 2. a) HER polarization curve (LSV) of the GC/LI, GC/Pt, GC/LI/Pt and-1 commercial Pt/C labelled GC/Nafion/Pt/C recorded at 5 mV.s in 0.5 M H₂SO₄ aqueous solution. d) The corresponding Tafel plots obtained from polarization curves.

Figure. 2a shows the HER polarization curve of GC/LI/Pt recorded in an acidic medium (0.5 M H₂SO₄), under argon atmosphere. For comparison, Pt electrodeposited onto GC (GC/Pt) and commercial Pt/C (GC/Pt/C) were also investigated. We used the Nafion on the commercial electrode (Pt/C), whereas the other investigated electrodes were used as-prepared.

Figure. 2a indicates that all the generated electrodes exhibit a good redox catalytic activity towards HER when compared to GC/LI. Deeper analysis shows that the onset potentials for GC/Pt and GC/LI/Pt are comparable and their values are about 10 mV, which is similar to commercial Pt/C. In addition, the required overpotential to achieve a current density of 10 mA.cm⁻² is about 65 mV on the GC/Pt, while a lower value of 52 mV is observed for GC/LI/Pt, which is comparable to commercial Pt/C sample (55 mV). Interestingly, at higher current density (-60 mA.cm⁻²), the required overpotential on GC/LI/Pt is 74 mV, while 84 mV and 130 mV are required on commercial Pt/C and GC/Pt, respectively. The HER is a typical example of two electron transfer reaction with an intermediate (Hads) and can follow two pathways, either the Volmer – Heyrovsky or the Volmer–Tafel mechanism [13].

Tafel slope investigation has also been used to compare the reaction rate and the mechanism (Fig. 2b). The GC/LI/Pt Tafel slope value is about 25 mV.dec⁻¹ which is lower than those measured with GC/Pt and commercial (Pt/C) electrodes (37 mV.dec⁻¹ and 31 mV.dec⁻¹, respectively). This result suggests that the GC/LI/Pt displays the best HER kinetics and that the HER follow a Volmer–Tafel mechanism. In addition, the two Hads recombination is the rate determining step. Overall, the electro-catalytic investigations suggest that the grafted ionic layer enhances the HER performance of the electrodeposited Pt.

This behaviour demonstrates a synergetic effect between the Pt and the ionic layer. The latter could be linked to the LI layer role during the Pt electrochemical growth and to the nitrogen (within the imidazolium, electron-rich dopant) presence, which may facilitate the electron transfer and or affect the Hads.

Paladium

As Pt, the similar experiments were performed using Pd as electrocatalyst. Fig. 3a displays the HER polarization curves of the GC/Pd, GC/LI/Pd and commercial Pd NPs (labelled GC/Nafion/PdNPs) as well as the corresponding Tafel plots (Fig. 3b).

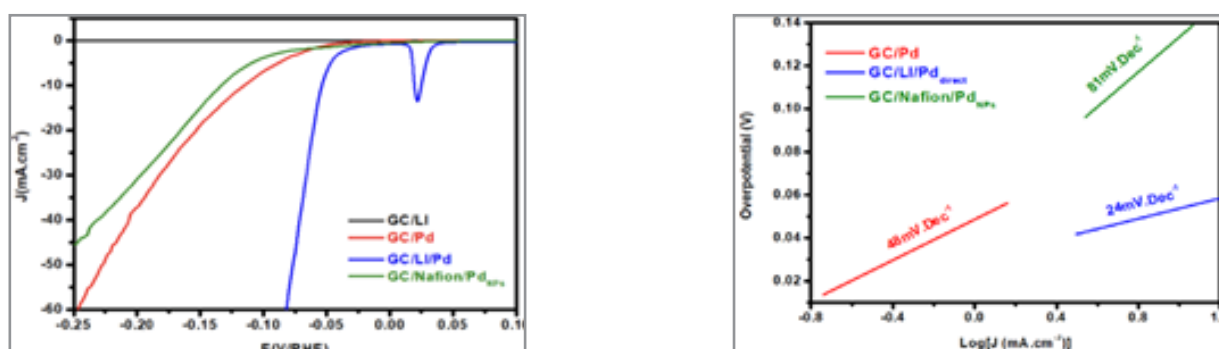


Figure. 3. a) HER polarization curve (LSV) of the GC/LI, GC/Pd, GC/LI/Pd and -1 commercial Pd (labelled GC/Nafion/PdNPs) recorded at 5 mV.s in 0.5 M H₂SO₄ aqueous solution. b) The corresponding Tafel plots obtained from polarization curves.

The GC/LI/Pd exhibits the best HER performance with a low onset potential (-10 mV) and low overpotential (53 mV) to

reach a current density of 10 mA.cm⁻², which is lower than those measured with GC/Pd (114 mV) and GC/Nafion/PdNPs

(133 mV). The GC/LI/Pd displays electrocatalytic performances similar to that recorded on commercial Pt/C. This was also confirmed by Tafel plots (Fig. 3b). Indeed, the GC/LI/Pd exhibits a Tafel slope of 24 mV.dec⁻¹, which is lower than that of GC/Nafion/PdNPs (81 mV.dec⁻¹) and GC/Pd (48 mV.dec⁻¹). More interestingly, the GC/LI/Pd Tafel slope is even lower than the value measured with commercial electrode Pt/C (31 mV.dec⁻¹) and similar to that observed with GC/LI/Pt (25 mV.dec⁻¹). This value indicates that the HER on GC/LI/Pd occurs through a Volmer-Tafel mechanism with Tafel reaction as the rate determining step. Furthermore, compared with the literature data, the GC/LI/Pd is among the best Pd-based electrocatalysts as attested by a lower overpotential value ($\eta = 53$ mV) [14]. Overall, these results clearly confirm the dual role of the attached ionic layer, which acts as a binder for the Pd electrocatalyst and also enhances the HER performance and kinetics.

Conclusions

In summary, this work demonstrates the ionic layer electrochemical grafting leading to imidazolium moieties onto GC and its further functionalization through electrochemical deposition of metallic nanoparticles (Pt and Pd). The electrolytic activities towards HER of the generated modified electrodes confirm that the HER activity and kinetic on Pt and Pd nanoparticles are enhanced in the ionic layer presence. More interestingly, the GC/LI/Pd exhibits excellent HER performances superior of commercial electrode (Pt/C). This enhancement is probably related to the dual role of the attached ionic layer, which acts as a host-guest platform for the electrocatalyst and also to the synergetic effect between the ionic layer and the NP's. This approach is a promising route to generate polymer binder free electrocatalyst and to enhance the intrinsic electrocatalytic performances of a given catalyst.

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