Hydrogen storage in hybrid of layered double hydroxides/reduced graphene oxide using spillover mechanism

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Abstract

New efficient hydrogen storage hybrids were fabricated based on hydrogen spillover mechanism, including chemisorptions and dissociation of H₂ on the surface of layered double hydroxides (LDH) and diffusion of H to reduced graphene oxide (rGO). The structures and compositions of all of the hybrids (LDHs/rGO) have been verified using different methods including transmission electron microscopy, X-ray diffraction spectroscopy, infrared spectroscopy and Brunauer–Emmett–Teller analysis. Then, the abilities of the LDHs/rGOs, as hydrogen spillover, were investigated by electrochemical methods. In addition, the LDHs/rGOs were decorated with palladium, using redox replacement process, and their hydrogen spillover properties were studied. The results showed that the hydrogen adsorption/desorption kinetics, hydrogen storage capacities and stabilities of Pd[#]LDH/rGOs are better than Pd/rGO. Finally presence of different polymers (synthesis with monomers, 4-aminophenol, 4-aminothiophenol, *o*-phenylenediamine and *p*-phenylenediamine) at the surface of the Pd[#]LDH/rGOs on hydrogen storage were studied. The results showed that presence of *o*-phenylenediamine and *p*-phenylenediamine improves the kinetics of the hydrogen adsorption/desorption

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and increase the capacity of the hydrogen storage.

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1. Introduction

Hydrogen, as a source of energy, has several advantages including ease of synthesis, its non-polluting nature and its abundance. A suitable method for storage of hydrogen is important in vehicular applications. One of cost effective hydrogen storage system is proton exchange membrane fuel cell for on board vehicular applications. Development of new hydrogen storage materials is one of the major technological barriers and challenges [1–4].

Hydrogen spillover arises in hydrogen catalyzed reactions on supported metal catalysts. Dihydrogen molecules dissociate on the metal part of the catalyst. Some hydrogen atoms remain attached to the metal, whilst others diffuse to the support. [5–7]. An applicable spillover sorbent should: (a) permit the diffusion of H_2 or H atoms in a well-dispersed pore lattice, (b) have most of the interior pore surface area disposable to encounter with spillover H_2 or H, and (c) be lightweight to maximize the gravimetric hydrogen uptake. Thus, the hydrogen uptake in mesoporous carbon and metal-organic frameworks (MOFs), which have suitable surface area and proper porosity and low-density, can be augmented substantially by hydrogen spillover [8–11].

Graphene, due to its high surface area and chemical durability, has a potential as a hydrogen adsorbent. Experimental and theoretical studies confirm that graphene can adsorb hydrogen by physisorption and/or chemisorption mechanisms. Reduced graphene

oxide (rGO) has unrivalled properties to serve as a hydrogen storage material. Therefore, this property is improved by combining rGO with selective nanostructures and compounds. Two approaches can be used to improve the surface of rGO: (i) via creation of nanometer-sized pores to create deeper potential wells and dramatically raise the surface area for adsorption and (ii) by doping with some elements (such as Al, Li, Ca, V, Fe, Ni, Cu, Zn, Pd, Pt, Ru, and TiO₂) to increase its interaction ability with the hydrogen substrate [12–21].

In this work, modified layered double hydroxides (LDHs) have been extensively used to develop functional nanomaterials. A combination of physisorption of hydrogen in porous materials (using rGO), chemisorption of hydrogen molecules at Al-M (M: Cu, Ni, Zn) decorated with Pd and finally formation of metal hydrides, were used to increase the advantages and reduce the drawbacks of the new nanocomposite as a hydrogen sorbent. Here, the feasibilities and capabilities of the LDH/rGOs and Pd#LDH/rGOs (using redox replacement) as new sorbents were investigated for hydrogen storages at room temperature and pressure. Finally presence of different polymers including 4-aminophenol, 4-aminothiophenol, *o*-phenylenediamine and *p*-phenylenediamine at the surface of the Pd#LDH/rGOs were studied on their hydrogen storage capacities too. The results showed that the hydrogen adsorption/desorption kinetics, hydrogen storage capacities and stabilities of Pd#LDH/rGOs are better than Pd/rGO.

2. Experimental

2.1. Materials and reagents

Potassium tetrachloropalladate 98% (CAS Number: 10025-98-6), aluminum nitrate $\geq 98\%$ (CAS Number: 7784-27-2), copper nitrate $\geq 98\%$ (CAS Number: 10031-43-3),

zinc nitrate 98% (CAS Number: 10196-18-6), nickel nitrate $\geq 98.5\%$ (CAS Number: 13478-00-7), graphite 99.99% (CAS Number: 7782-42-5), ethylene glycol 99.8% (CAS Number: 107-21-1), 4-aminophenol 98% (CAS Number: 123-30-8), 4-aminothiophenol 97% (CAS Number: 1193-02-8), *o*-phenylenediamine 98% (CAS Number: 95-54-5) and *p*-phenylenediamine 99% (CAS Number: 106-50-3) were purchased from Sigma-Aldrich. All other chemicals were of analytical grade and purchased from Merck. Double distilled water was used for preparation of all the solutions.

2.2. Characterization methods

Fourier-transform infrared (FT-IR) spectra of the LDH hybrids were recorded using a JASCO 680 spectrophotometer over the wavenumber range of 400–4000 cm^{-1} . Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) (XL, Philips) were employed to characterize Pd#Al-M/LDH-rGOs and Al-M/LDH-rGOs (Cu, Ni, and Zn) morphologies and to explore the presence of different LDH-rGOs. Transmission electron microscopy (TEM) was performed using a Philips CM120. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ultra-high vacuum (UHV) set-up equipped with the concentric hemispherical analyzer and VG Microtech twin anode. XR3E2 X-ray source was used as incident radiation. X-ray diffraction (XRD) analysis was carried out with a Bruker D8/Advance X-ray diffractometer and with Cu- K_{α} radiation. A high performance volumetric physisorption apparatus at 77 °K Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) were used to investigate the real surface of different LDHs before and after redox replacement of the M with Pd. To determine the LDHs and the graphitization degree of rGO, thermogravimetric analysis (TGA) and derivative thermogravimetry

(DTGA) were performed using Rometric simultaneous thermal analysis. The heating program was performed in a temperature range from 30 to 850 °C with a heating rate of 10 °C min⁻¹.

Electrochemical analysis was performed by means of electrochemical galvanostatic measurement, Model PGSTAT 30 potentiostat/galvanostat (Eco-Chemie, the Netherlands), that was controlled by a microcomputer at ambient temperature and in 0.50 mol L⁻¹ H₂SO₄ as an electrolyte. Three-electrode cell set-up consists of a working electrode, which is made up of a glassy carbon electrode covered by different modified-LDHs (after redox replacement and finally after polymerization), a reference Ag/AgCl electrode and a Pt-wire as a counter electrode was used. Data were acquired and processed using GPSE computrace software 4.9.007 and FRA computrace software.

2.3. Synthesis of exfoliated graphene oxide and reduced graphene oxide

Modified Staudenmaier method was used to prepare graphene oxide (GO). Graphite powder (with a purity of 99.99% and particle size of 70 µm) was oxidized to GO at room temperature by chemical treatment. For this purpose, graphite (1.0 g) was added into a mixed solution containing conc. sulfuric acid (20 mL), conc. nitric acid (10 mL) and potassium chlorite (10.0 g). The mixture was stirred for 100 h. The resulting mixture was filtered, rinsed with 5.0 wt% HCl aqueous solution, and washed with water until the pH of the filtrate was neutral. The solid product was dried at room temperature. Finally, the obtained graphene oxide was dispersed in water (1.0 mg mL⁻¹), which was put in an ultrasonic bath for 2 h, to convert it to exfoliated graphene oxide (EGO) [22].

The reduction of EGO to rGO was performed as follows: 100 mL of EGO suspension (1.0 mg mL⁻¹) was prepared in double distilled water. The suspension was kept at 0 °C then five times of NaBH₄ (ratio to rGO, w/w) was added dropwise to the

suspension to reduce the EGO to reduced graphene oxide. The resulting suspension was filtered and washed with water several times. Finally, it was dried at room temperature [23].

2.4. Decoration of Pd nanoparticles on rGO

Pd-nanoparticles were deposited on rGO sheets by chemical reduction method using potassium tetrachloropalladate (K_2PdCl_4) in ethylene glycol–water (2/1, v/v) solution. In a typical procedure, 100 mg of rGO plus 80 mg of K_2PdCl_4 was dispersed in 100 mL of double distilled water. It was then added into 200 mL of ethylene glycol in a 500-mL flask. To uniformly disperse rGO in the ethylene glycol–water solution, the mixture was ultrasonically treated for 1 h. The reaction mixture was then stored at 100 °C for 12 h under constant stirring. During this time, Pd nanoparticles were decorated on rGO (Pt-rGO). Finally, the solid produced, Pt-rGO, was filtered and washed with water several times. The resulting product was dried in a vacuum desiccator at 60 °C for 12 h [23].

2.5. Preparation of LDHs-rGO hybrids and the hydrogen sorbents

Al-M/LDH-rGOs (M: Ni, Cu, Zn) were synthesized via ultrasonic irradiation as a simple, green and fast method. For preparation of Al-M/LDH-rGO, first 0.070 g of rGO was dispersed in an aqueous solution (2.06 mL) containing 9.9 mmol NaOH. Subsequently, 1.4 mL of a mixture solution of 2.80 mmol of $M(NO_3)_2 \cdot 6H_2O$ (where M: Ni, Cu, Zn) and 1.40 mmol $Al(NO_3)_3 \cdot 9H_2O$ was added to the above mixture. The resulting black suspension was stirred at 60 °C for 2 h under nitrogen atmosphere. The mixture was sonicated for 2 h under nitrogen atmosphere. The solid was recovered and

washed with double distilled water several times and finally dried under vacuum at 80 °C for 12 h [24].

Four different Al-M/LDH-rGO hybrids were prepared by adding 0.070 g, 0.140 g, 0.350 g, and 0.700 g of rGO in the presence of constant amount of Al-M/LDH precursor concentration. Moreover, both rGO and EGO were used to synthesize Al-M/LDH-rGO and Al-M/LDH-EGO under the same conditions.

To prepare the hydrogen sorbents, 2.50 mg of Al-M/LDH-rGO (M: Ni, Cu, Zn) was added into 1.0 mL water and the solution was sonicated for 15 min to prepare an ink. After cleaning a glassy carbon electrode (GCE) surface, the prepared ink (10 μ L) was dropped on the surface of GCE and it was dried at room temperature. To achieve Pd deposition at Al-M/LDH-rGOs, different LDH modified-GCE were immersed into 2.0 mmol L⁻¹ K₂PdCl₄ in 0.1 mol L⁻¹ H₂SO₄ solution (to allow the spontaneous reaction of surface M atoms with Pd(II) ions). Finally different monomers such as 4-aminophenol, 4-aminothiophenol, *p*-phenylenediamine and *o*-phenylenediamine were electropolymerized on the surface of the modified electrodes (Pd#Al-M/LDH-rGO). The electropolymerization was performed in a solution containing 0.20 mol L⁻¹ H₂SO₄ and 0.50 mol L⁻¹ of each of the monomers and potential cycling was run between -0.50 and 1.50 V at 50 mV s⁻¹ for 20 cycles [25]

3. Results and discussion

3.1. Physical characterization of the LDHs and characterization of the Pd#Al-M/LDH-rGO

Different methods including TEM, FE-SEM, EDS, XRD, FT-IR, TGA and BET were used to investigate the characteristics of M-Al/LDH-rGOs.

Fig. 1A shows the FT-IR spectra of the hybrid of Al-Ni/LDH-rGO with different ratios (wt%) of Al-Ni/LDH vs. rGO (100, 35, 20, and 10% w/w). The rGO characteristic peaks appeared at 3412, 1717, 1584, 1231 and 1050 cm^{-1} , which are attributed to O-H stretching, carbonyl C=O stretching, aromatic C=C stretching, epoxy C-O stretching and alkoxy C-O stretching. These results are in agreement with the previous reports on rGO [26]. In pure Al-Ni/LDH (Fig. 1A), the broad peak centered at about 3469 cm^{-1} is attributed to the O-H stretching vibration of water molecules in the interlayer. The peak at 1429 cm^{-1} is attributed to nitrate ions bound to Ni metal in C_{2v} symmetry. Furthermore, the absorption band below 700 cm^{-1} is ascribed to the characteristic peak of Ni-O and Al-O vibrations in the lattice of LDH [27]. According to these spectra, all bands due to the presence of both Al-Ni/LDH and rGO are observed. In addition, with increasing the amount of rGO, the characteristic peak around 1700 cm^{-1} is increased. Fig. 1B shows FT-IR spectra for different LDHs (Al-M/LDH-rGO, M: Ni, Cu, Zn) and the results for all of the LDHs showed the same properties too. **“Here Fig. 1”**

XRD patterns of rGO, Al-M/LDH and the hybrids of Al-M/LDH-rGOs (M: Ni, Cu, Zn) are presented in Fig. 2. The XRD pattern of rGO exhibits a sharp peak at 24.5° demonstrating the oxidation of graphite to EGO and then reduction. In addition, this is indicating inter planar spacing of (002) at about 0.85 nm, which is much larger than that of pristine graphite (0.34 nm). The width of the peak is attributed to a turbostratic arrangement of graphene stacked sheets. The diffraction peaks including (003), (006), (012), (015) and (018) planes of typical hydrotalcite-like pure Al-M/LDH are observed. The XRD pattern of hybrid of Al-M/LDH-rGO is almost identical to pure LDH. These results confirm that the LDH is well anchored on the rGO sheets and overlap with the rGO peak ($2\theta = 26.1$) [28]. **“Here Fig. 2”**

204 The morphologies and structures of the Al-M/LDH-rGOs (M: Ni, Cu, Zn) are
 205 investigated by FE-SEM and TEM too. Fig. 3 shows FE-SEM of Al-Zn/LDH-rGO (3A-
 206 a), Al-Ni/LDH-rGO (3B-a), and Al-Cu/LDH-rGO (3C-a) and also shows TEM images of
 207 Al-Zn/LDH-rGO (3A-b), Al-Ni/LDH-rGO (3B-b), and Al-Cu/LDH-rGO (3C-b). FE-
 208 SEM images show the LDH (that prepared by ultrasonic method) has roughly
 209 immobilized on the rGO sheets and also opening the sheets of rGO to rupture the LDH
 210 layers. Thus, porous structure is formed over the whole hybrid domain. These TEM
 211 images confirm that small platelets of LDH attached to the surface of rGO and most of
 212 the LDH platelets have oriented face on the graphene substrate. The thicknesses of the
 213 LDH platelets are around at 20-30 nm (according to the XRD results). This is due to the
 214 fact that during the synthesis, the positively charge of LDH sheets interact with the
 215 negatively charged rGO leading to immobilization of the LDHs between the rGO sheets
 216 [24]. **“Here Fig. 3”**

217 The BET surface area and the pore structures of the fabricated sorbents were
 218 characterized via N₂ adsorption and desorption isotherm at 77 K by a surface area
 219 analyzer. The surfaces area and pores diameter of the produced porous catalysts are
 220 summarized in Table 1. The results show that the surface area of the hybrids are as Al-
 221 Zn/LDH-rGO > Al-Ni/LDH-rGO > Al-Cu/LDH-rGO. On the other hand, the results
 222 showed that after redox replacement between the divalent cations in the LDH with Pd,
 223 the surface area of the prepared Pd#Al-Ni/LDH-rGO is decreased (Table 1). This is due
 224 to the blocking of micropores or mesopores of the rGO or LDH by the palladium
 225 nanoparticles. Moreover, to confirm the hybridization of LDH-rGO with palladium
 226 nanoparticles, palladium nanoparticles were decorated on the surface of rGO. Then, the
 227 surface area of Pd/rGO was determined using BET. The results showed that the surface
 228 area of Pd/rGO was lower than Al-M/LDH-rGO. These results confirm that doping of

the LDH causes increasing in the surface area vs. doping of one metal (Pd/rGO). The BET investigation also classifies the pore sizes in different sorbents. According to IUPAC, pores sizes are classified into micropores, mesopores and macropores with pore diameter up to 2, from 2 to 50, and > 50 nm, respectively. The Barret–Jayner–Halenda technique for quantifying mesopore volumes of LDHs showed that they have pores diameter between 2.18 and 3.6 nm. The results of our studies indicated that the pore characteristics of the different Al-M/LDH-rGO, before and after redox replacement, have the same diameter sizes. The results are given in Table 1, confirms that the pores diameter for all of the sorbents are as mesopore.

238

239 **Table 1**

240 Surface area and the porosity of the porous synthesized solid state sorbents.

Sample	Surface area (m ² g ⁻¹)		Pore diameter (nm)		
	Langmuir	BJH adsorption	BJH desorption	BJH adsorption	BJH adsorption
Al-Ni/LDH-rGO	50.9	109.65	127.52	2.67	2.18
Al-Cu/LDH-rGO	55.70	104.05	119.13	2.74	3.6
Al-Zn/LDH-rGO	53.90	150.71	174.44	2.75	2.43
Pd#Al-Ni/LDH-rGO	45.52	102.82	98.73	2.78	2.46
Pd/rGO	22.3	51.83	60.50	2.76	2.18

241

242 TGA curves of Al-M/LDH-rGOs in nitrogen were recorded. All of the samples
 243 exhibited three distinct weight loss steps: the first weight loss from 100 to 250 °C is due
 244 to the release of the adsorbed water and water contents in the hybrids; the second weight

loss from 300 to 450 °C corresponds to removal of nitrate anions and the dehydroxylation of the LDH layers; and finally different reactions could be occurring at higher temperature (500–700°C). The weight loss in nitrogen is ascribed to the reduction of M^{2+} to M^0 by carbon [23]. The TGA residues of the Al-Zn/LDH-rGO, Al-Ni/LDH-rGO and Al-Cu/LDH-rGO hybrid materials were 25, 21 and 18 wt.%, respectively.

Redox replacement reaction was used to prepare Pd-modified Al-M/LDH-rGO as the hydrogen sorbents. Divalent cations of M in Al-M/LDH-rGOs were used for the redox replacement with Pd^{2+} . Divalent cations cannot directly react with $PdCl_4^{2-}$, whereas H^+ ions are crucial for the redox replacement of Pd [23]. For example, Al-Ni/LDH-rGO was put in a solution of 2.0 mmol L^{-1} K_2PdCl_4 (in the presence of 0.1 mol L^{-1} H_2SO_4) over different times followed by rinsing with double distilled water and its cyclic voltammetric response was recorded between –0.30 to +1.50 V in 0.1 mol L^{-1} H_2SO_4 . The results (just for Al-Ni/LDH-rGO) of the oxidation/reduction peaks of Pd nano-clusters at different times, for the redox replacement, are shown in Fig. 4A. These results of our study confirmed that Pd nanoclusters were fabricated at the surface of Al-M/LDH-rGO electrodes. The redox replacement of Ni^0 with Pd^{2+} can result in the formation of a mono- or sub-monolayer of Pd on the surface of the modified electrodes.

X-ray photoelectron spectroscopy is employed to confirm the elemental composition and oxidation states of the divalent metal cations in the LDH and formation of palladium nanoparticles on the LDHs surface. For example, the recorded XPS spectra show a distinct evolution of Ni peak in Al-Ni/LDH-rGO. The de-convoluted high-resolution Ni XPS spectrum of Al-M/LDH-rGO shows six different types of Ni configurations on the Al-M/LDH-rGO. Spectral fitting of the XPS data measured for Al-Ni/LDH-rGO showed all three species (Ni metal, NiO and Ni hydroxide), as shown in Fig. 4B. Existence of nickel in state of Ni^0 , can suggests that Pd^{2+} ions are partially

reduced to Pd⁰ due to electron transfer from Ni metal in the LDH sheets, since the reduction of Pd²⁺ is thermodynamically favored for redox replacement. The challenge of galvanic exchange is solved by the analysis of the XPS spectrum of nickel at the LDH sheets. Thus, the redox replacement process took place on Al-M/LDH-rGO (M: Ni, Cu, Zn) and Pd#Al-M/LDH-rGO are synthesized. “Here Fig. 4”

The compositions of Al-M/LDH-rGOs before and after redox replacement were analyzed using EDS. For example, the results of Al-Ni/LDH-rGOs are given in Table 2 that clearly shows the presence of C, O, Al, and Ni elements with their weights percent before and after the redox replacement. Moreover, the compositions of Pd#Al-Cu/LDH-rGO and Pd#Al-Zn/LDH-rGO before and after redox replacement were analyzed by EDS and are given in Table S-1 in the supplementary material. These results showed the reduce weights percent of the divalent cations (Zn, Ni, Cu) and increases the weight ratio of Pd after the redox replacement. These results confirmed that Al-M/LDH-rGO and Pd#Al-M/LDH-rGO hybrid were successfully synthesized. Moreover, the compositions of Pd/rGO were also characterized with EDS and the results are given in Table 3. These results confirm the presence of C, O, and Pd in the composition of Pd-rGO. On the other hand, a comparison between the amount of Pd on the surface of Pd/rGO and Pd#Al-M/LDH-rGO revealed that presence of Pd at Pd/rGO was three times of Pd at Pd#M-Al/LDH-rGO.

Table 2

EDS results for the synthesized hydrogen storage sorbent, Al-Ni/LDH-rGO, before and after redox replacement.

Element	Line	After redox replacement		Before redox replacement	
		Atomic%	Conc. wt%	Atomic%	Conc. wt%
C	Ka	72.19	57.35	69.91	57.14
N	Ka	1.10	0.79	2.27	1.62
O	Ka	11.12	9.20	11.48	9.35
Al	Ka	7.50	13.37	8.26	11.97
Ni	Ka	3.89	8.30	8.08	20.1
Pd	La	4.19	10.98	--	--
		100.00	100.00	100.00	100.00

Table 3

EDS results for Pd-rGO.

Element	Conc. wt%	Line	Atomic%	Conc. wt%
C	49.03	Ka	71.11	49.03
O	10.78	Ka	13.44	10.78
Pd	40.19	Ka	15.45	40.19
	100.00		100	100.00

3.2. Electrochemical behaviors of the Al-M/LDH-rGO and Pd#Al-M/LDH-rGO and effect of different polymers on their hydrogen storage

To further investigate the hydrogen storage properties of the Al-M/LDH-rGO and Pd#Al-M/LDH-rGO, cyclic voltammetry is used too. In the anodic pathway scan, hydrogen desorption plateau appeared at about -0.12 V, which can be attributed to the following reaction:

In the cathodic pathway scan, a hydrogen adsorption plateau appeared at about -0.23 V, which can be attributed to the following reaction:

The cyclic voltammetry results confirm that hydrogen adsorption/desorption active sites are present in Pd#Al-M/LDH-rGO. It is also noted that the same current for both the cathodic and anodic currents indicates the excellent reversibility of the solid state sorbent. In this work, all voltammetric results were normalized based on the EDS results.

In order to obtain the best conditions for the maximum hydrogen capacity and stability of Pd#Al-M/LDH-rGO for hydrogen storage, the effect of various experimental parameters including type of divalent cations in the preparation of LDH (Ni, Zn, Cu), presence of rGO or EGO in the preparation of the hybrid LDH/graphene, weight percent of the LDH (M+Al) on rGO, time of the redox replacement of M with Pd and type of the monomer for the polymerization were studied.

Our goal was the use of the hydrogen storage sorbents at room temperature and atmospheric pressure. For this condition, monolayer or sub-monolayer of Pd was decorated at Al-M/LDH-rGO using redox replacement. Then, *o*-phenylenediamine was used to electropolymerize Pd#Al-M/LDH-rGO. First of all the effects of rGO and EGO on the hydrogen storage capacities in the synthesis of Al-M/LDH were investigated. For this purpose, Al-M/LDH-rGO and Al-M/LDH-EGO (10.0% w/w LDH) were synthesized. After the redox replacement and electropolymerization of the modified electrode with *o*-phenylenediamine, typical CVs of Pd#Al-M/LDH-rGO/*o*-phenylenediamine and Pd#Al-M/LDH-EGO/*o*-phenylenediamine in $0.50 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ were recorded at a scan rate of 20 mV s^{-1} . The results showed that the hybrid of LDH-rGO has high current density (10 times) vs. the hybrid of LDH-EGO (Fig. 5A). In hydrogen spillover mechanism, after dissociation of H_2 on the surface of Pd#LDH, the

created H is transferred to rGO or EGO. Therefore, the surface area and interlayer distance of rGO or EGO are very important. The results showed that rGO has higher capacity to storage H atoms than EGO.

The weight percent ratio of M+Al/rGO (100, 35, 20, and 10% w/w) is the second factor that can increase hydrogen sorption capacities of the LDH hybrid. For this purpose, after preparation of the modified electrode and redox replacement and electropolymerization of the modified electrode with *o*-phenylenediamine, cyclic voltammogram of them were recorded in 0.50 mol L⁻¹ H₂SO₄ with a scan rate of 20 mV s⁻¹. As can be seen in Fig. 5B, with increasing the percent of rGO in the hybrid of LDH/rGO, both anodic and cathodic currents densities of the adsorption/desorption of hydrogen were increased and the maximum current density was observed in 10.0% w/w of the LDH on rGO. The improved electrochemical performance of Al-M/LDH-rGO is attributed to the chemical and electronic coupling between the Al-M/LDH and rGO sheets. Due to the unique electrical properties of graphene as an additive, by incorporating rGO sheets with the LDH, the conductivity of Al-M/LDH could be improved. Moreover, rGO provides a large surface area for good dispersion of Al-M/LDH-rGO, forming much smaller Al-M/LDH-rGO, as compared with the pure M-Al/LDH. Smaller Al-M/LDH-rGO sheets in the hybrid favor the exposure of more active sites for the solid state sorbent. Thus, much faster electron transfer and high real surface area of the Al-M/LDH-rGO are the key factors contributing to the greatly enhanced hydrogen sorbent capacity.

One other factor that can increase hydrogen sorption capacity is element substitution. Therefore, type of divalent cations in the preparation of the LDHs (Ni, Zn, and Cu) were studied. It is well known that Al-M/LDH-rGO belongs to A₂B type hydrogen storage alloys, in which Al represents the A side elements while M represents

the B side elements (with the EDS results 2:1 Al:M). They act differently from each other. Generally, A side elements are Al, La, Ce, Pr, Nd, Sm, whereas B side elements are Co, Cu, Ni, Zn, Mn, and Zr, those can improve the gaseous and electrochemical kinetics of hydriding/dehydriding. For this purpose, different modified electrodes based on Al-M/LDH-rGO (Ni, Zn, Cu) (after redox replacement and electropolymerization) were prepared and typical CVs of the electrodes were recorded in H₂SO₄ solution (Fig. 5C). As can be seen, Pd#Al-Zn/LDH-rGO-*o*-phenylenediamine shows the highest current density [29]. This process can be justified by the result of a BET and TEM of the different LDH, because Al-M/LDH-rGO shows biggest surface area and best morphology.

Finally, the redox replacement between the divalent cations in the preparation of LDHs (Ni, Zn, and Cu) and Pd should be optimized. The divalent cations in LDHs cannot directly react spontaneously with PdCl₄²⁻. For example, Al-Cu/LDH-rGO was put in a solution of 2.0 mmol L⁻¹ K₂PdCl₄ (in the presence of 0.1 mol L⁻¹ H₂SO₄) over different times followed by rinsing with distilled water and its voltammogram was recorded in 0.5 mol L⁻¹ H₂SO₄. Cyclic voltammograms of Pd#Al-M/LDH-rGO in 0.5 mol L⁻¹ H₂SO₄ showed oxidation/reduction peaks. These peaks confirm that the Pd monolayer is fabricated at the surface of Al-M/LDH-rGO. As the CVs show (Fig. 5C), by replacement of Pd with Ni, Cu and Zn (using redox replacement process) the peaks current for the hydrogen adsorption/desorption increased (increases the capacity of the hydrogen sorption) and the peaks potential shifted to more positive direction (increasing in the adsorption/desorption kinetics), in comparison to Al-M/LDH-rGO (M: Ni, Zn and Cu). Moreover, to confirm the performance of LDHs as solid state hydrogen sorbents, performance of Pd/rGO vs. Pd#Al-M/LDH-rGO was investigated too. To comprise the hydrogen sorbent ability of Pd/rGO vs. Pd#Al-M/LDH-rGO, all the obtained currents

(from cyclic voltammetry for different amount of Pd) were normalized. The results showed that the hydrogen capacity of the electropolymerized Pd#Al-M/LDH-rGOs (M = Ni, Zn, Cu) were higher than electropolymerized Pd/rGO, whereas the hydrogen adsorption/desorption kinetics for the Pd/rGO was the same as the Pd#Al-M/LDH-rGO.

“Here Fig. 5”

A few polymers such as polyaniline and polypyridine have been used to enhance the hydrogen storage capacity of hydrogen sorbents. The structures of these polymers are suitable to interact with molecular hydrogen by hydrogen bonding in the polymer structure, and increase the hydrogen storage capacity [30, 31]. Depending on the charge of the hydrogen species (H^+ , H_2 , H^0 , H^-) a combination of metallic, covalent, H-bonding, ionic, and van der Waals interactions could exist within and between the polymer chains and with the chemical hydrides (AlH_x), metal hydrides (M: Ni, Cu, Zn) and Pd nanoparticle. In this study, the effect of different polymers, synthesized with their monomers such as 4-aminophenol, 4-aminothiophenol, *p*-phenylenediamine and *o*-phenylenediamine, were investigated on the hydrogen capacity and kinetics of the hydrogen storages. The results of our studies showed that presence of synthetic polymers such as by *p*-phenylenediamine and/or *o*-phenylenediamine at Pd#Al-M/LDH-rGO increase the capacity and kinetics of the hydrogen storages at room temperature and pressure, whereas polymers based on 4-aminophenol and 4-aminothiophenol cause a reduction the capacity and kinetics of the hydrogen storages. For example, the results for Pd#Al-Zn/LDH-rGO are shown in Figs. 6A, 6B, 6C and 6D. **“Here Fig. 6”**

On the other hand, to confirm the results of the hydrogen capacity and kinetics of Pd#Al-M/LDH-rGO-*o*-phenylenediamine, *o*-phenylenediamine was electro-polymerized at the surface of an unmodified glassy carbon electrode, and then cyclic voltammogram was recorded in the potential range of -0.31 to $+1.00$ V in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution.

The results did not show any adsorption/desorption peaks in the potential range of -0.40 to 0.00 V vs. Ag/AgCl (Fig. 7A). Moreover, the same investigations were done for Cu-Al/LDH-rGO before and after its electropolymerization with *o*-phenylenediamine. The results also show low adsorption/desorption peaks in the potential range of -0.40 to 0.00 V (Fig. 7B). Finally, cyclic voltammogram of Pd#Al-Cu/LDH-rGO (between -0.30 to $+1.00$ V) was recorded before and after its electropolymerization with *o*-phenylenediamine. The results showed that Pd#Cu-Al/LDH-rGO before electropolymerization has low hydrogen adsorption/desorption current density, whereas after electropolymerization, the hydrogen adsorption/desorption current density increases too much (Fig. 7C). All the obtained results confirm that combination of LDH/rGO, Pd nanoparticles and *o*-phenylenediamine produce high performance hydrogen sorbent.

“Here Fig. 7”

3.3. Spillover mechanism

Synergetic effect of Pd#Al-M/LDH-rGO-*o*-phenylenediamine could be explained by spillover effect. In many cases, spillover effect has been observed for H_2 storage in carbon-based materials like reduced graphene oxide and/or exploited graphene oxide-*o*-phenylenediamine. Pd nanoparticle is a typical component that can dissociate H_2 to $2H$ (spillover effect). Moreover, Al was used to form chemical hydride and M (Ni, Cu and Zn) was used to form metal hydride [32]. Thus, hydrogen can chemisorbed and physisorbed on the surface of Pd#Al-M/LDHs and rGO, respectively. Therefore, when Pd#Al-M/LDH decorated on rGO, the hydrogen capacity of the sorbent significantly increased, because rGO and/or hybrid of LDHs/rGO has high surface area and more carbon atoms with sp^2 hybrid vs. EGO and/or LDHs/rGO [31].

Moreover, in Pd#Al-M/LDH (M: Ni, Cu, Zn) three kind of metals were used to prepare the hydrogen sorbent to have synergic effect on hydrogen spillover (Al was used

to form chemical hydride and M was used to form metal hydride and monolayer of Pd to form metal cluster to dissociate hydrogen to H^{*}). Cyclic voltammetry results for Pd/rGO (before electropolymerization) show very small peaks current for adsorption/desorption of hydrogen because of its slow kinetic, while for Pd#Al-M/LDH-rGO the peaks current for adsorption/desorption of hydrogen are more noticeable (Fig. 8). This result confirm that hydrogen can better chemisorbs on the surface of Pd#Al-M/LDH and storage done at nearly the same temperature with spillover effect.

“Here Fig. 8”

3.4. Linear polarization and electrochemical impedance spectroscopy

The polarization curves, obtained in 0.5 mol L⁻¹ H₂SO₄ illustrated the kinetics of hydrogen adsorption/desorption on the surface of the solid state sorbents. The linear parts of the steady-state polarization curves indicated that hydrogen production and then storage over the solid state sorbent were kinetically controlled by charge transfer. The Tafel equation is described as follows [33]:

$$\eta = (2.303RT/\beta nF) \cdot \log(i_0) - (2.303RT/\beta zF) \cdot \log(i) = \alpha + b \cdot \log(i) \quad (3)$$

where η (V) represents the applied overpotential, b (V dec⁻¹) is the Tafel slope, I (A) is the resulting current, α is the intercept related to the exchange current i_0 (A) and R is the universal gas constant. β , n and F are the symmetric factors, number of exchange electrons and the Faraday constant, respectively [34]. Using Eq. 3, the Tafel slope and the exchange current, as electrochemical parameters, can be measured. The apparent exchange current, i_0 , provides information about the catalytic activity of the electrodes. As shown in Table 4, the kinetic parameters for Pd#Al-M/LDH-rGO and Pd/rGO after electropolymerization with *o*-phenylenediamine showed that all of the solid state hydrogen sorbents have fast kinetic with Volmer-Tafel mechanism.

Although electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry are quite different experimental techniques (ac versus dc), the results obtained should be comparable. Linear sweep voltammetry gives the dependence of the overall hydrogen adsorption/desorption rate (measured by current density) on the applied overpotential. The result of EIS analysis showed that the overall rate of the hydrogen adsorption/desorption is related to both the charge-transfer

Table 4

Kinetic parameters obtained from steady-state Tafel curves for the hydrogen storages in 0.5 mol L⁻¹ H₂SO₄ aqueous solution.

Solid state sorbent	(Tafel slope) ⁻¹ (Vdec ⁻¹)	A
Pd#Al-Zn/LDH-rGO	28.7	0.87
Pd#Al-Cu/LDH-rGO	29.2	0.79
Pd#Al-Ni/LDH-rGO	27.5	0.8
Pd/rGO	32.3	0.74

resistance, R_{ct} , and to the hydrogen adsorption resistance, R_p . Hence, combining these two resistances in a series of R_{ct} and R_p and using the ohm's law, it is possible to plot the semi-logarithmic dependence of the hydrogen adsorption/desorption rate. The activity of the solid state hydrogen sorbents were also studied using EIS. Figs. 9A and 9B show Nyquist plots (I_{mZ} imaginary impedance against R_{eZ} real impedance) obtained at Pd#Al-M/LDH-rGO electrodes before and after electropolymerization with *o*-phenylenediamine at an overpotential of 200 mV in 0.50 mol L⁻¹ H₂SO₄ solution. In general, after electropolymerization of *o*-phenylenediamine on the surface of Pd#Al-M/LDH-rGO, the

charge transfer resistance of the hydrogen adsorption/desorption was reduced. This result showed the positive effect of *o*-phenylenediamine at the surface of the solid state sorbent. Moreover, the effect of divalent cations (used in the synthesis of LDHs), and Pd nanoparticles decorated on rGO were investigated too. The results showed that the charge transfer resistance of the solid states are as: Pd#Al-Zn/LDH-rGO < Pd#Al-Ni/LDH-rGO < Pd#Al-Cu/LDH-rGO < Pd/rGO. These results confirm the existence of LDHs and two and three-valent cations increases the kinetic of the electron transfer [35].

“Here Fig. 9”

3.5. Stability of the hydrogen sorbents

Another important feature of a hydrogen sorbent is its high durability. To assess this, the prepared Pd#Al-M/LDH-rGO modified electrodes were used to record 500 successive cyclic voltammograms in potential range of -0.35 to 1.00 V vs. Ag/AgCl, in 0.5 mol L⁻¹ H₂SO₄. The results showed that the current of the hydrogen adsorption/desorption at Pd#Al-M/LDH-rGO were reduced to about 73% to its initial value (desorption of hydrogen). These results are shown in Figs. 10A, 10B and 10C, and confirm that the Pd/LDHs hybrids have high stability as solid state hydrogen sorbents.

In continuing our studies, presence of some polymers at the surface of Pd#Al-Cu/LDH-rGO on the stability of modified LDHs was investigated. To assess this, the prepared Pd#Al-Cu/LDH-rGO modified electrode after electropolymerization with *p*-phenylenediamine and/or *o*-phenylenediamine, were used to record 250 successive cyclic voltammograms in potential range of -0.35 to 1.00 V vs. Ag/AgCl, in 0.5 mol L⁻¹ H₂SO₄. The results showed that the current of hydrogen adsorption/desorption at Pd#Al-Cu/LDH-rGO-*p*-phenylenediamine was reduced to 25% of its initial value, whereas for Pd#Al-Cu/LDH-rGO-*o*-phenylenediamine, it was reduced to 94% of its initial value

(Figs. 10D and 10E). These results showed that electropolymerization of the modified LDHs with *o*-phenylenediamine produced a highly stable solid state hydrogen sorbent.

“Here Fig. 10”

In addition, the influence of type of divalent cations (in the LDHs) on the stability of hydrogen storage were also studied. For this purpose, Pd#Al-M/LDH-rGO-*o*-phenylenediamine modified glassy carbon electrodes (M: Ni, Zn, Cu) were prepared and their stabilities in the hydrogen adsorption/desorption were studied using cyclic voltammetry with 500 successive cycles in the potential range of –0.32 to 1.00 V. The results are shown in Fig. 11, and confirm that all of the LDHs have good stabilities for hydrogen adsorption/desorption. The current of hydrogen adsorption/desorption at Pd#Al-M/LDH-rGO-*o*-phenylenediamine was reduced to just 87% of its initial value (Fig. 11, A, B and C). On the other hand, to check the effect of the existence of different LDHs on the stability of the hydrogen storage, the stability of Pd/rGO (after immobilization on the surface of a GCE and its electropolymerization with *o*-phenylenediamine) was studied using cyclic voltammetry with 200 successive cycles in the potential range of –0.32 to 1.00 V. The results of Pd/rGO showed that the hydrogen adsorption/desorption current reduced to 10% of its initial current (Fig. 11D). This result confirms that existence of the LDHs on rGO increases the stability of hydrogen storage in this solid state sorbent. **“Here Fig. 11”**

4. Conclusion

Here, solid state hydrogen sorbents were prepared based on hybrid of layered double hydroxides Al-M (M: Cu, Ni, Zn) and rGO. These sorbents have three features; they consist of absorbent at a porous material (hybrid of LDH/rGO), formation of chemical hydride (Al-H) and formation of metal hydride (Zn, Cu, Ni). Moreover,

palladium is well known as an effective catalyst for reactions related to hydrogen and as a hydrogen-storage metal and at room temperature and pressure conditions. Therefore, a combination of LDHs and Pd nanoparticles (using redox replacement) was used to prepare the hydrogen sorbents (Pd#Al-M/LDH-rGO). To improve the kinetics of hydrogen adsorption/desorption and the sorption capacities, they were covered with different polymers such as 4-aminophenol, 4-aminothiophenol, *o*-phenylenediamine, and *p*-phenylenediamine. Then, the hydrogen storage parameters were investigated. The results showed that presence of *o*-phenylenediamine, and *p*-phenylenediamine at the surface of Pd#Al-M/LDH-rGO increased the kinetics of the hydrogen adsorption/desorption and increases the capacity of the hydrogen storage. On the other hand, presence of some functional groups such as oxygen and/or sulfur on the monomer (such as 4-aminophenol and 4-aminothiophenol) reduces the kinetics of the hydrogen adsorption/desorption and reduces the capacity of the hydrogen storage. Finally, combination of physisorption in the porous materials (rGO) with chemisorption in the chemical hydride (Al), and presence of the metal hydride (Cu, Zn, Ni) with interstitial hydrides (Pd) are the key advantages of the proposed hydrogen sorbents with high stabilities, and high adsorption/desorption kinetics.

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671 **Legends for the figures:**

672 **Fig. 1.** A): FT-IR spectrum of Al-Ni/LDH-rGO with different percent of LDH on rGO
673 as: (a) 100%, (b) 35%, (c) 20%, (d), 10%, B): FT-IR spectrum of (a): Al-Zn/LDH-rGO,
674 (b): Al-Ni/LDH-rGO, and (c): Al-Cu/LDH-rGO.

675 **Fig. 2.** XRD pattern of (a): rGO, (b): Al-Zn/LDH-rGO, (c): Al-Cu/LDH-rGO, and (d):
676 Al-Ni/LDH-rGO.

677 **Fig. 3.** FE-SEM images of A-a): Al-Zn/LDH-rGO; B-a): Al-Cu/LDH-rGO; and C-a): Al-
678 Ni/LDH-rGO. TEM images of A-b) Al-Zn/LDH-rGO; B-b): Al-Cu/LDH-rGO; and C-b):
679 Al-Ni/LDH-rGO.

680 **Fig. 4.** A): Cyclic voltammograms of Al-Ni/LDH-rGO after redox replacement in
681 different time in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution with a scan rate of 50 mV s^{-1} . B): High
682 resolution XPS data for Ni in Al-Ni/LDH-rGO and the curve fitting.

683 **Fig. 5.** A): Cyclic voltammograms of Pd#Al-Cu/LDH-rGO-*o*-phenylenediamine with
684 different percent of LDH on rGO as: (a) 100%, (b) 35%, (c) 20%, and (d) 10%. B):
685 Cyclic voltammograms of (a) Pd#Al-Zn/LDH-rGO-*o*-phenylenediamine, and (b) Pd#Al-
686 Zn/LDH-EGO-*o*-phenylenediamine. C): Cyclic voltammograms of (a) Pd#Al-Zn/LDH-
687 rGO-*o*-phenylenediamine, (b) Pd#Al-Ni/LDH-rGO-*o*-phenylenediamine, and (c) Pd#Al-
688 Cu/LDH-rGO-*o*-phenylenediamine. Conditions: in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution with a
689 scan rate of 20 mV s^{-1} .

690 **Fig. 6.** Cyclic voltammograms of Pd#Al-Zn/LDH-rGO after electropolymerization with
691 A): *o*-Phenylenediamine, B): *p*-Phenylenediamine, C): *p*-Aminophenol, and D): *p*-
692 Aminothiophenol. Conditions: in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution with a scan rate of 20 mV s^{-1} .
693 ¹.

694 **Fig. 7.** Cyclic voltammograms of A): GCE after electropolymerization with *o*-
695 phenylenediamine, B) Al-Cu/LDH-rGO-*o*-phenylenediamine, and C): Pd#Al-Cu/LDH-
696 rGO-*o*-phenylenediamine in 0.5 mol L⁻¹ H₂SO₄ solution with a scan rate of 20 mV s⁻¹.

697 **Fig. 8.** Cyclic voltammograms of A): Pd#Al-Cu/LDH-rGO, B): Pd#Al-Ni/LDH-rGO, C):
698 Pd#Al-Zn/LDH-rGO, and D): Pd/rGO, in 0.5 mol L⁻¹ H₂SO₄ solution with a scan rate of
699 20 mV s⁻¹.

700 **Fig. 9** A): EIS (Nyquist plots) of (a) Pd/rGO, (b) Pd#Al-Cu/LDH-rGO, (c) Pd#Al-
701 Ni/LDH-rGO, and (d) Pd#Al-Zn/LDH-rGO. B): EIS of (a) Pd#Al-Zn/LDH-rGO, and (b)
702 Pd#Al-Zn/LDH-rGO-*o*-phenylenediamine. Conditions: in 0.5 mol L⁻¹ H₂SO₄ solution at
703 a potential of -300 mV vs. Ag/AgCl.

704 **Fig. 10.** 1th (a) and 200th (b) successive cyclic voltammograms of A): Pd#Al-Cu/LDH,
705 B): Pd#Al-Ni/LDH-rGO, C): Pd#Al-Zn/LDH-rGO, D): Pd#Al-Zn/LDH-rGO-*o*-
706 phenylenediamine, and E): Pd#Al-Cu/LDH-rGO-*p*-phenylenediamine. Conditions: in 0.5
707 mol L⁻¹ H₂SO₄ solution with a scan rate of 20 mV s⁻¹.

708 **Fig. 11.** Five hundred successive cyclic voltammograms of A): Pd#Al-Zn/LDH-rGO-*o*-
709 phenylenediamine, B): Pd#Al-Cu/LDH-rGO-*o*-phenylenediamine, and C): Pd#Al-
710 Ni/LDH-rGO-*o*-phenylenediamine. D): 200 successive cyclic voltammograms of
711 Pd/rGO-*o*-phenylenediamine. Conditions: in 0.5 mol L⁻¹ H₂SO₄ solution with a scan rate
712 of 20 mV s⁻¹.

Figure 1

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Figure 3