Hydroxyapatite supported Pd_xIn_{100-x} as a novel electrocatalyst for high-efficiency glucose electrooxidation

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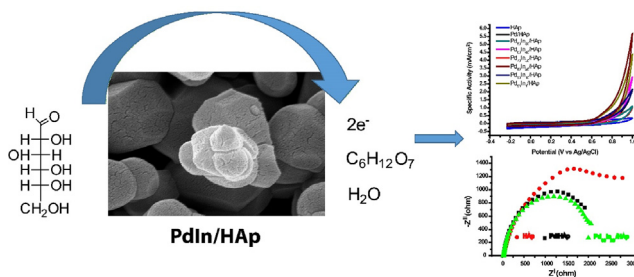[d] *Department of Chemical Engineering, Faculty of Engineering and Architectural Science, Eskisehir Osmangazi University, Eskişehir, 26040, Turkey*
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HIGHLIGHTS

- PdIn/HAp catalysts with varying atomic molar ratios were synthesized by the $NaBH_4$ reduction method.
- $Pd_{80}In_{20}$/HAp exhibited excellent electrocatalytic activity for glucose electrooxidation.
- $Pd_{80}In_{20}$/HAp showed long-term stability as a DGFC anode catalyst.

GRAPHICAL ABSTRACT

ABSTRACT

Fuel cells are a very good candidate to provide energy conversion with green technology. Glucose is used as a fuel in fuel cells since it is easily available and has a high energy density. Herein, hydroxyapatite (HAp) was synthesized by precipitation method, and the sodium borohydride ($NaBH_4$) reduction method was used to fabricate HAp supported PdIn (PdIn/HAp) alloy anode catalysts at varying atomic molar ratios for glucose electrooxidation. Structural, crystallographic, and morphological properties of the PdIn/HAps were determined with X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), Brunauer-Emmett-Teller (BET) analysis, transmission electron microscopy (TEM), and inductively coupled plasma mass spectrometry (ICP-MS). Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and chronoamperometry (CA) were employed for the electrocatalytic activity and stability of PdIn/HAps toward glucose electrooxidation. The results show that HAp has a boosting effect for PdIn alloy towards glucose electrooxidation. $Pd_{80}In_{20}$/HAp showed 2.6 times

higher electrocatalytic activity than Pd/HAp, and it is the most active and stable catalyst in this study with a specific activity of 5.64 mA/cm^2.

Abbreviations

HAp	Hydroxyapatite
EIS	Electrochemical İmpedance Spectroscopy
DGFC	Direct Glucose Fuel Cell
XRD	X-Ray Powder Diffraction
CV	Cyclic Voltammetry
BET	Brunauer–Emmett–Teller
CNF	Carbon Nanofiber
RGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-Ray Analysis
ICP-MS	Inductively Coupled Plasma – Mass Spectrometer
CA	Chronoamperometry
GCE	Glassy Carbon Electrode
PEMFC	Polymer Electrolyte Membrane Fuel Cell
TEM	Transmission Electron Microscopes
MWCNT	Multi-Walled Carbon Nanotubes
CNF	Carbon Nanofiber
KB	Ketjenblack Carbon
r.d.s	Rate Determining Step
R	Resistance
W	Warburg Element
Q	Constant Phase Element
S_{BET}	BET Surface Area
C	Concentration
D	Diffusion Coefficient
A	Surface Area

Introduction

Fuel cells are devices that convert chemical energy into electrical energy through electrochemical reactions [1]. Their use in portable electronic devices, transportation, and constant power generation has become quite common. Automobile companies have produced prototype automobile models that provide energy from fuel cells [2,3]. Cost reduction is an important problem for fuel cells to become a widely used commercial product. However, proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells have promising performance for commercialization [4–6]. Apart from these, more studies should be conducted on liquid-feed fuel cells namely hydrazine [7,8], methanol [9,10], ethanol [11,12], glycerol [13,14], formate [15,16], formic acid [17,18], dimethyl ether [19], and glucose [20,21].

The negative effects of fossil fuel sources on environment and the human health have accelerated the research of readily available and environmentally friendly materials for fuel cells [22–24]. Glucose is a good alternative for use as a fuel in fuel cells due to its unique properties among liquid fuels such as dimethyl ether, hydrazine, methanol, formic acid, and ethanol. Because glucose is a neutral carbon source, it can be stored and transported more safely than other fuels [25,26]. The fact that glucose is not toxic [27], flammable [28], and volatile [29] also reduces the storage and transportation costs of glucose. It is also a very good energy provider, releasing 24 e$^-$ in the complete oxidation of glucose [30,31]. The anode, cathode, and overall reactions for direct glucose fuel cells (DGFCs) are given in Eqns. (1)–(3) [32].

$$C_6H_{12}O_6 + 2OH^- \rightarrow C_6H_{12}O_7 + H_2O + 2e^- \tag{1}$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{2}$$

$$C_6H_{12}O_6 + \frac{1}{2}O_2 \rightarrow C_6H_{12}O_7 \tag{3}$$

The kinetics of glucose electrooxidation reaction occurring at the anode is vital for improving the efficiency of DGFCs. The reaction kinetics slowing down, especially at low temperatures reduces the performance of the fuel cell. The performances of noble metals namely Pt and Pd as anode catalysts for DGFCs have been investigated before. However, many studies have reported that monometallic Pd and Pt are poisoned by carbonaceous intermediates formed during glucose electrooxidation [33–35]. Researchers have benefited from the synergistic effects of binary anode catalysts to increase poisoning tolerance. Accordingly, the electrocatalytic performance of anode catalysts for glucose electrooxidation have been reported such as NiCuO/ITO [36], NiO$_x$/Gr/GCE [37], Ir/CNT [38], Pt/CNT [39], NiO$_x$/GC [40], ITO/TiO$_2$/Co$_3$O$_4$ [41], Co@NCD [42], Mg$_{65}$Bi$_{35}$ [43], BiAu/MWCNT [44], NiCu/GC [45], Pt$_9$Bi$_1$/C [46], Pd/C$_3$N$_4$–C [47], NiCo/rGO [1], AuPtPd [48], Bi–Co–S [49], Pd$_3$Cu–B/C [29], NiFe/Graphene [50], PtNiCu/GC [51], Fe–Ni–Co/C [28], PdPt/Graphene [27], and PdIn/C [52]. There is extensive sensor literature as well as fuel cell applications on glucose electrooxidation. In recent years, Tsiakaras group investigated PdCo/KB [53] and Pd/N-3D [54] electrocatalysts for the detection of glucose co-existing with ascorbic acid, uric acid, and dopamine in the human body. This research group proposed mechanisms for glucose electrooxidation on Pt, Pd, Au, Cu, Co, and Ni, and the mechanism of glucose electrooxidation on Pd is shown in Scheme 1 [55,56]. Researchers reported that glucose electrooxidation activity is strongly dependent on charge and mass transport between metal (II) and metal (III).

These multi-metal catalysts have been reported to have higher electrocatalytic activity and stability than monometallic catalysts. Researchers have attributed the increased

electrochemical performance to bifunctional, electronic, and ensemble effects or a combination of these effects. In addition, many studies have emphasized the effect of atomic molar ratios of metals on their electrocatalytic activities. Chai et al. informed that the mass activity of the Pd_3Cu-B/C electrocatalyst for glucose electrooxidation was 0.105 A/mg Pd, which was approximately 15 times higher than compared to Pd/C. Researchers reported that the d band center of palladium shifted towards its optimum value with the addition of Cu [29]. Another factor affecting the performance of catalysts is the selection of support materials with which the particles can be well dispersed. As far as we know, carbon derivatives such as CNT, rGO, and XC-72 are frequently used as support materials for glucose electrooxidation. Researchers have reported that these carbon derivatives are preferred as support materials owing to their electrically conductive and high surface areas [57,58]. Since the carbon derivatives do not interact strongly enough with the metal nanoparticles loaded on them, the catalytic activity is negatively affected [59]. Hydroxyapatite (HAp) is a good alternative to the aforementioned carbonaceous support materials due to its abundance in nature and its hydroxyl-rich structure to which metal nanoparticles can bind [60]. The most important properties of HAps that allow them to be used as support materials are their high adsorption capacity and ion exchange capacity [61] as well as the easily adjustable Ca/P ratio [62]. HAps have an important potential as catalyst support material due to their easy design, flexible structures, thermal stability, adjustable surface acidic/basic properties, and bifunctionality because of acidic/basic sites [63,64]. Cui et al. reported that the Pd/HAp catalyst showed approximately two times higher electrocatalytic activity compared to Pd/C for ethanol electrooxidation and the enhancement in catalytic activity was attributed to the removal of adsorbed carbonaceous compounds by hydroxyl groups on the HAp surface [59]. Safavi et al. also informed that hydroxyl groups adsorbed on HAp surface in an alkaline medium increased electrocatalytic activity by preventing CO-like poisoning [65]. HAps have been frequently used as a component of composite materials for glucose sensors and medical applications. However, the performance of HAp, which has a high tolerance to CO poisoning with its hydroxyl-rich chemical structure, as an anode catalyst support material for glucose electrooxidation has not been reported yet.

In this study, PdIn/HAp anode catalyst with varying atomic molar ratios was prepared by the $NaBH_4$ reduction method and its electrocatalytic performance was investigated for the glucose electrooxidation reaction. XRD, XPS, BET, SEM-EDX, TEM, and ICP-MS methods were used to characterize PdIn/HAp electrocatalysts. The electrochemical performance of the synthesized catalysts was determined by electrochemical impedance spectroscopy (EIS), chronoamperometry (CA), and cyclic voltammetry (CV).

Materials and methods

Reagents

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), Indium (III) chloride ($InCl_3$), Potassium tetrachloropalladate (II) (K_2PdCl_4), di-ammonium hydrogen phosphate (($NH_4)_2HPO_4$), ammonia, and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich and used for the synthesis of PdIn/HAps catalysts. All chemicals used for the preparation of PdIn/HAp are in analytical grade. Nafion 117 (5%), potassium hydroxide (KOH, 90%) and D-glucose ($C_6H_{12}O_6$, 98%) were utilized for electrochemical tests.
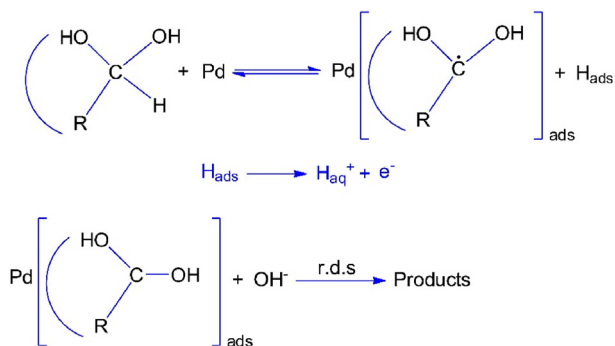
Preparation of hydroxyapatite powder

The synthesis of Indium (III) chloride ($InCl_3$) doped hydroxyapatite (HAp) powders were effectuated by a co-precipitation method. The reagents, di-ammonium hydrogen phosphate (S2) and calcium nitrate tetrahydrate (S1) were dissolved in DI to prepare the solutions with a certain molar ratio (Ca/P = 1.67). Ammonia was added drop by drop into the S2 solution and continuously stirred for 1 h. After 24 h of aging, the final solution (S3) was filtered to obtain a wet cake. Afterward, the filtered Indium (III) chloride ($InCl_3$) doped HAp was dried in an oven at 200 °C to remove the excess water and ammonia. The sintering process for the resulting powders was applied at 1100 °C in the air for 1 h. A schematic representation of HAp preparation is shown in Scheme 2.
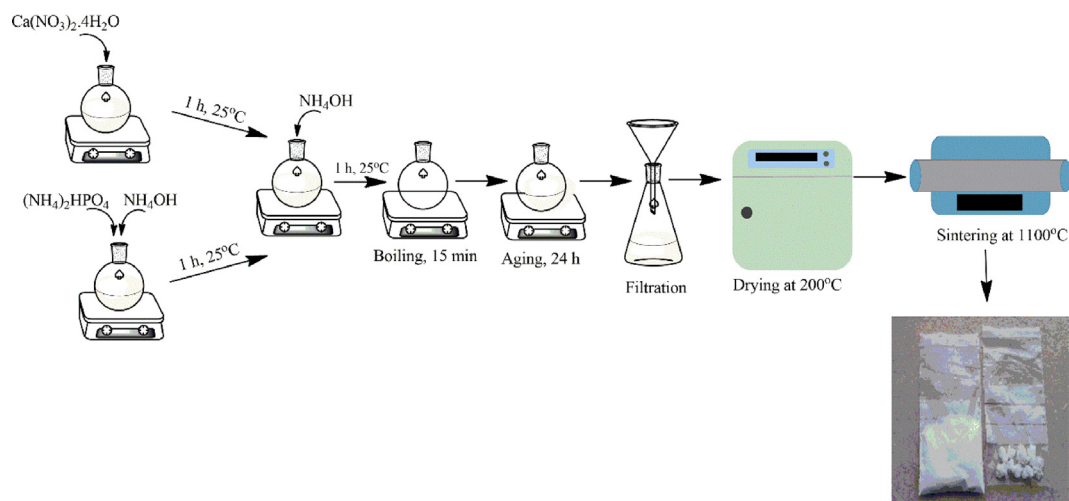
Preparation and characterization of PdIn/HAp

10% PdIn/HAps at varying metal compositions were prepared with the $NaBH_4$ reduction method [66]. PdIn/HAp catalysts were synthesized at Pd:In atomic molar ratios of 99:1, 90:10, 80:20, 70:30, 60:40, and 50:50. As reported in our previous study, metal salts containing Pd and In were stirred in distilled water, and 100 mg of HAp was put in the solution and stirred at room temperature for 60 min [67]. Metal salts were reduced by adding $NaBH_4$ dropwise to the solution in a 1:15 M metal/$NaBH_4$ ratio. The solution, which was stirred for an additional 30 min, was filtered, washed, and dried at 85 °C for 12 h.

PANalytical Empyrean X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å) was used to determine the crystal

Scheme 1 – Mechanism of glucose electrooxidation on Pd catalyst.

Scheme 2 — Synthesis procedure of HAp.

phases of the obtained catalysts. Hitachi HighTech HT7700 TEM device was used to observe the average particle size and particle distribution, and the TEM images were analyzed with ImageJ software. The Pd/In molar metal ratios of PdIn/HAp electrocatalysts were determined via the ICP-MS method with Agilent 7800 device.

Electrochemical evaluation

CHI-660E potentiostat with a conventional three electrodes system was utilized for the determination of glucose electrooxidation performance of as-synthesized catalysts. Glassy carbon (GCE), Pt wire, and Ag/AgCl were used as working, counter, and reference electrodes, respectively. Specific activities of all catalysts in this study were normalized to the geometric area of the working electrode. All electrochemical experiments were performed in 1 M KOH+ 0.5 M Glucose solution. For the preparation of the glassy carbon electrode, 5 mg of PdIn/HAp and 1 ml of Nafion 117 solution were ultrasonicated to obtain catalyst ink. 5 μl of catalyst ink was transferred to the surface of GCE and dried. The electrochemical activity of PdIn/HAps was investigated using CV

between the potential range of -0.23-1 V at 50 mV/s scan rate. The stability of the catalysts was specified with CA at 50 mV/s scan rate and 1 V potential. The electrocatalytic activity and charge transfer resistance of PdIn/HAps were determined from the EIS profile at 1 V potential.

Results and discussion

Characterization of PdIn/HAp

The crystallinity of the synthesized catalysts was determined by the XRD method. The particle size distributions and average particle size of PdIn/HAp were analyzed by TEM. XPS and BET methods were used to determine surface oxidation property and N_2 adsorption-desorption behavior of PdIn/HAp. Also, the atomic molar ratios of PdIn/HAps were investigated by ICP-MS.

Fig. 1 displays the XRD pattern of $Pd_{80}In_{20}$/HAp. The observed diffraction peaks of HAp in the XRD pattern are highly compatible with JCPDS data No: 09−432, and HAp is predominantly in the hexagonal crystalline phase [68]. Also,
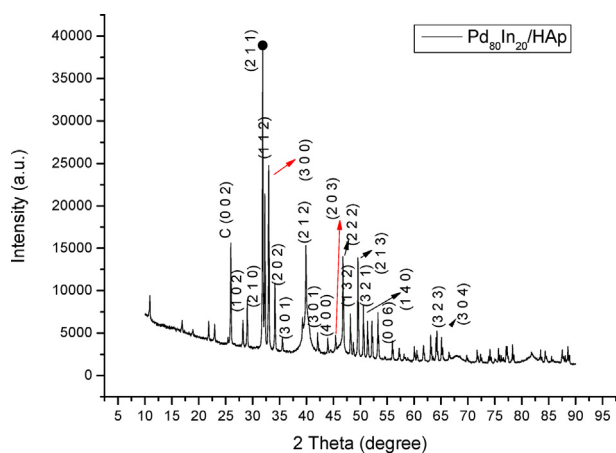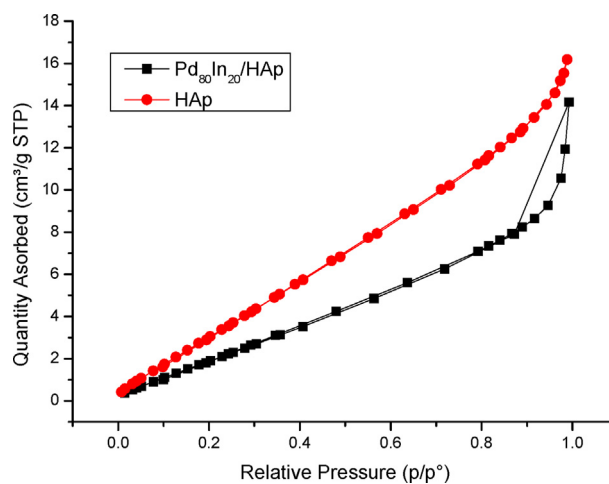

Fig. 1 — XRD pattern of $Pd_{80}In_{20}$/HAp.

Fig. 2 — BET isotherms of HAp and $Pd_{80}In_{20}$/HAp.

Table 1 — Results obtained from N_2 adsorption-desorption isotherms.

Electrocatalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
HAp	9.54	0.0220	6.04
$Pd_{80}In_{20}$/HAp	14.0	0.0253	6.27

the XRD pattern of plain HAp is given in Figure S1 and is used to label the diffraction peaks of Pd and In. The diffraction peaks of Pd distributed on the HAp were observed as shoulder peaks since they were located at similar 2Θ angles to the diffraction peaks of the HAp. The shoulder peaks observed at 2Θ angles of 40.0°, 46.9°, and 82.1° were attributed to Pd (1 1 1), Pd (2 0 0), and Pd (3 1 1) facets [69]. In addition, the diffraction peak observed at 2Θ of 39.2° is due to the In (1 1 1) peak [70]. The shifts observed in the characteristic diffraction peaks of face center cubic Pd (JCPDS card no. 05–0681) indicate that Pd is alloyed with In to form a new phase [71]. Moreover, the crystal size of $Pd_{80}In_{20}$/HAp was found to be 6.81 nm by the Scherer equation.

BET adsorption-desorption experiment was used to obtain the porosity and the surface area of HAp and PdIn/HAp. The parameters of pore structure and BET isotherms for HAp and $Pd_{80}In_{20}$/HAp were exhibited in Fig. 2 and Table 1. According to the UIPAC classification, plain HAp conforms to the type II isotherm, while the N_2 adsorption-desorption behavior of the $Pd_{80}In_{20}$/HAp catalyst could be explained by the type III isotherm (Fig. 2). The N_2 adsorption-desorption behaviors of HAp and $Pd_{80}In_{20}$/HAp catalysts were attributed to strong and
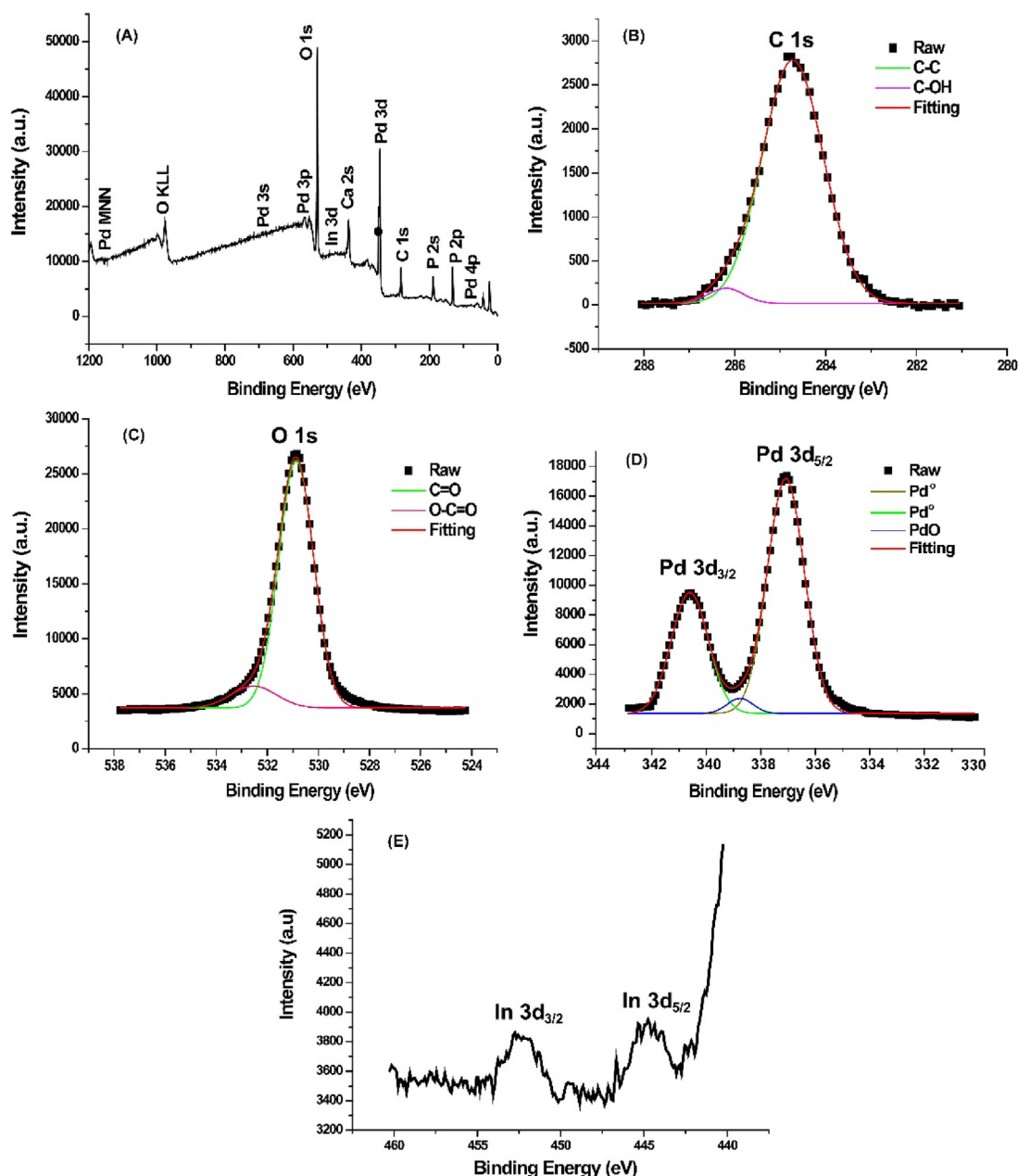

Fig. 3 — a) General spectrum, b) C 1s, c) O 1s, d) Pd 3d, and In 3d core-level XPS spectra of $Pd_{80}In_{20}$/HAp.

weak adsorbate-adsorbent interactions, respectively [72]. The increase in volume adsorbed at low relative pressures was attributed to the existence of micropores in the structure. In the BET isotherm of HAP, a second enhancement was observed after a relative pressure greater than 0.9, indicating the presence of macropores. For $Pd_{80}In_{20}/HAp$, the second enhancement was detected after 0.8 relative pressure. S_{BET}

values of HAp and $Pd_{80}In_{20}/HAp$ were found to be 9.54 and 14.0 m^2/g, respectively (Table 1).

The surface electronic state of $Pd_{80}In_{20}/HAp$ was examined by using XPS (Fig. 3). Peaks indicating the presence of Pd, In, Ca, P, and C was observed from the XPS general spectrum of the $Pd_{80}In_{20}/HAp$ catalyst (Fig. 3a). Calibration of binding energies for spectra was performed according to C 1s peak at 284.6 eV.
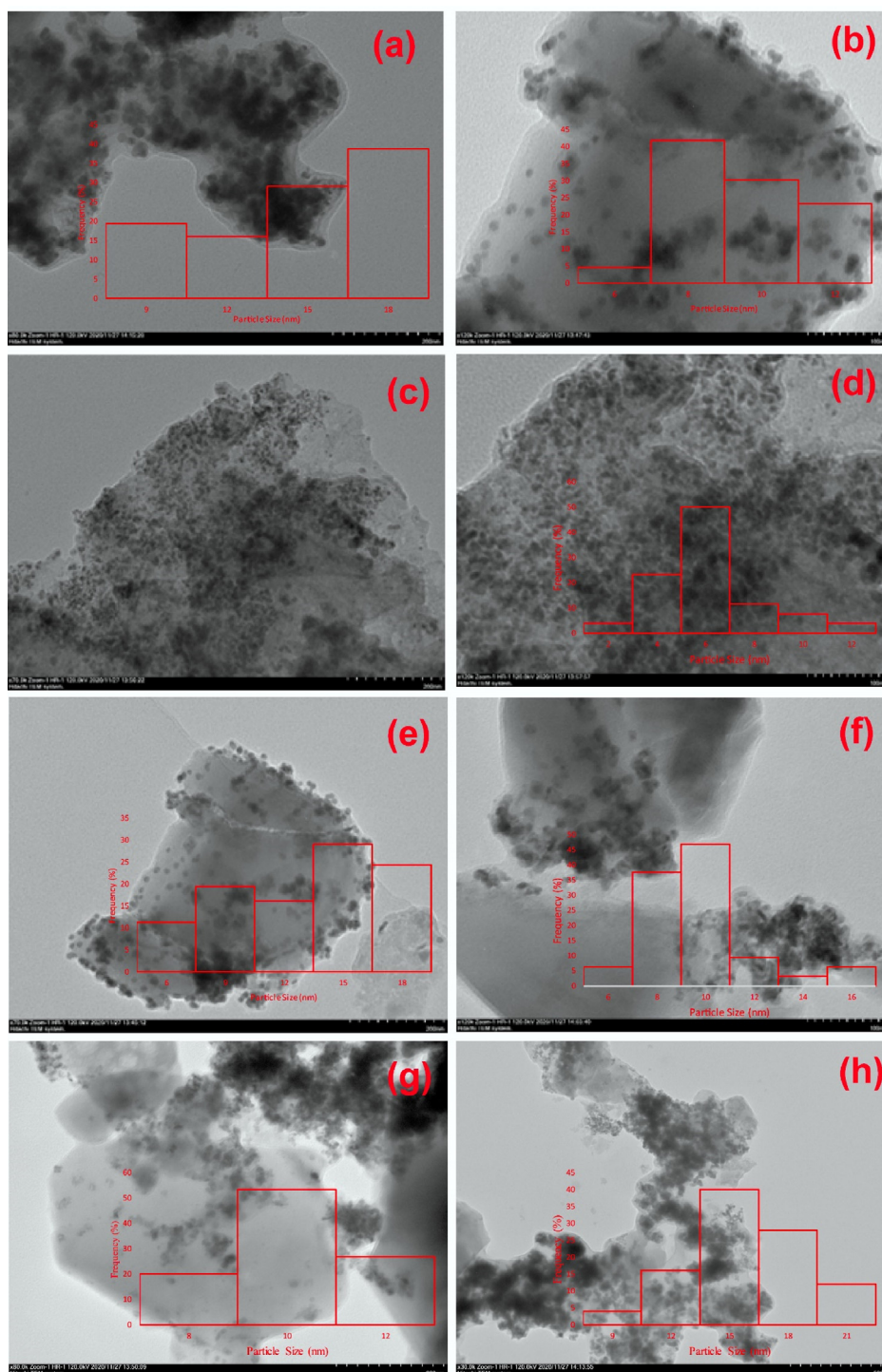

Fig. 4 — TEM images of $Pd_{80}In_{20}/HAp$.

The peaks detected at 284.6 and 286.1 eV binding energies were assigned to the presence of C−C and C−OH groups in the HAp structure (Fig. 3b) [73,74]. High-resolution XPS O 1s spectra obtained from $Pd_{80}In_{20}$/HAp displayed two deconvoluted peaks at binding energy of 530.8 and 532.4 eV associated with C=O and O−C=O [75] (Fig. 3c). Fig. 3d shows the high-resolution XPS spectrum of Pd. $Pd\ 3d_{3/2}$ and $Pd\ 3d_{5/2}$ were observed at binding energies of 340.6 and 337.3 eV and attributed to the presence of elemental Pd. Besides, the peak observed at 338.8 eV was assigned to the PdO form. It was concluded from the areas of the deconvoluted peaks that the Pd in the catalyst structure was predominantly in the form of Pd^o. XPS spectrum of core-level In 3d is presented in Fig. 3e. The peaks observed at the binding energies of 452.3 and 444.7 eV correspond to $In\ 3d_{3/2}$ and $In\ 3d_{5/2}$, respectively. It has been concluded from XPS results that the metals used were successfully reduced to their elemental forms by the $NaBH_4$ method.

TEM images showing the distribution of nanoparticles on the HAp and corresponding particle size histograms were shown in Fig. 4. Although a severe agglomeration was observed in Fig. 4a and g, it was determined that the particles were more homogeneously distributed on the HAp in other TEM images. The observed agglomeration is due to the very rapid reduction of metal salts by $NaBH_4$, which is used as a reductant. It is also evident from the particle size histograms that the particles are dispersed in a narrow size range. The average particle size was determined as 9.18 nm using ImageJ software.

Elemental distribution and morphology of $Pd_{80}In_{20}$/HAp were evaluated by performing SEM, EDX, and elemental mapping. Spherical nanoparticles were detected in the SEM image of $Pd_{80}In_{20}$/HAp (Fig. 5a−c). EDX results show that the $Pd_{80}In_{20}$/HAp catalyst contains P, Ca, O, Pd, and In in its structure (Fig. 5i). In addition, the distribution of O, P, and Ca in the structure of HAp was determined by elemental mapping analysis (Fig. 5d−h). The oxygen in the catalyst structure originates from the hydroxyl ions in HAp. Especially from Fig. 5f and g, it was observed that the Pd and In planes exhibited a uniform distribution on HAp support.

The atomic molar compositions of the PdIn/HAps were confirmed by ICP-MS and the results were given in Fig. 6. The molar Pd/In ratio of the $Pd_{50}In_{50}$/HAp, $Pd_{60}In_{40}$/HAp, $Pd_{70}In_{30}$/HAp, $Pd_{80}In_{20}$/HAp, $Pd_{90}In_{10}$/HAp, and $Pd_{99}In_1$/HAp catalysts were determined as 44.6/55.4, 57.3/42.7, 73.7/26.3, 77.8/22.2, 85.1/14.9, and 96.8/3.2, respectively. The fact that the metal ratios are almost the same as the targeted ratios indicates that the synthesis is successful in terms of obtained metallic molar ratios.

Electrochemical evaluation

The electrocatalytic performance of the PdIn/HAp catalysts for glucose electrooxidation was determined in 1 M KOH+0.5 M Glucose electrolyte at 50 mV/s scan rate by EIS, CV, and CA. The electrocatalytic performances of PdIn/HAps were compared with HAp and Pd/HAp.
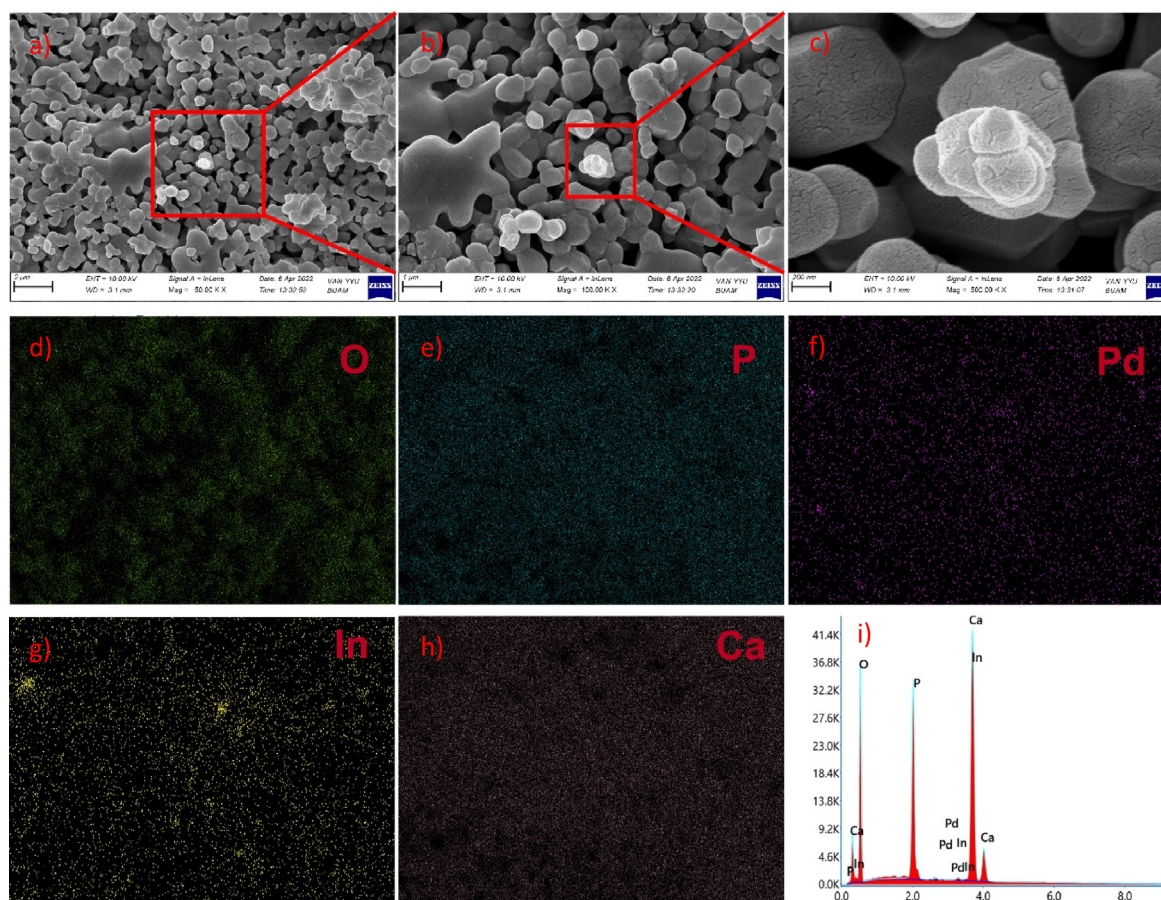

Fig. 5 − SEM images, elemental mapping analysis, and EDX analysis of $Pd_{80}In_{20}$/HAp.
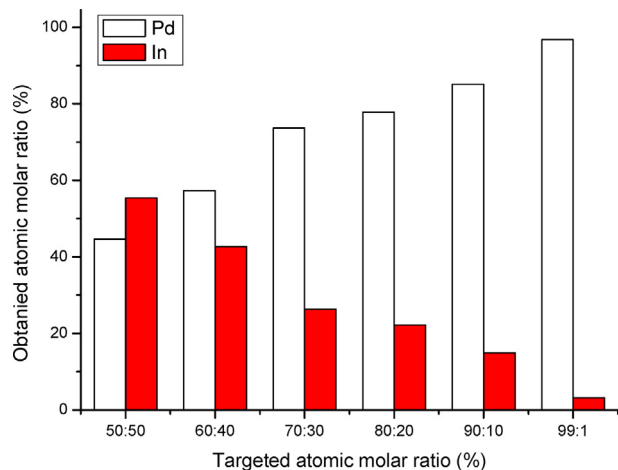
Fig. 6 – ICP-MS results of PdIn/HAps.

Glucose electrooxidation activity

Cyclic voltammograms of PdIn/HAp catalysts at varying atomic molar ratios in 1 M KOH and 1 M KOH + 0.5 M Glucose solutions were presented in Fig. 7. Cyclic voltammograms of In/HAp catalyst in 1 M KOH and 1 M KOH + 0.5 M Glucose solution are shown in Figure S2. As can be seen from Figure S2, the specific activity of the In/HAP catalyst toward glucose electrooxidation is 0.83 mA/cm^2. It is seen from Fig. 7a that all catalysts except HAp have a hydrogen adsorption-desorption region at the potential range of −0.023 V−0.07 V. In addition, a double layer region was observed in the potential range of 0.016−0.32 V for the electrocatalysts other than Pd$_{50}$In$_{50}$/HAp and Pd$_{60}$In$_{40}$/HAp [76]. The peak observed at 0.23 V potential in the reverse scan for the voltammogram of the Pd$_{70}$In$_{30}$/HAp catalyst was attributed to PdO reduction [77]. From the areas of voltammograms recorded in KOH solution, it is clearly seen that the electrochemically active surface areas of Pd$_{99}$In$_1$/HAp, Pd$_{80}$In$_{20}$/HAp, and Pd$_{60}$In$_{40}$/HAp electrocatalysts are higher than other electrocatalysts.

It is seen that the electrochemically active surface area of HAp increased with the addition of Pd (Fig. 7b). With the addition of Pd, the specific activity of HAp for glucose electrooxidation increased approximately 6 times. All synthesized anode catalysts were found to be active for glucose electrooxidation from the obtained specific activity values in 1 M KOH and 1 M KOH + 0.5 M Glucose solution (Table 2). Among the catalysts obtained by adding In to Pd/HAp, only the electrocatalytic activity of Pd$_{60}$In$_{40}$/HAp, Pd$_{80}$In$_{20}$/HAp, Pd$_{90}$In$_{10}$/HAp, and Pd$_{99}$In$_1$/HAp catalysts increased. The deviation of the distance between the d band center of Pd and the Fermi level from its optimum value for glucose electrooxidation is one of the main reasons for the decrease in the specific activities of other catalysts [69]. Pd$_{80}$In$_{20}$/HAp displayed the highest electrocatalytic activity with a specific activity of 5.64 mA/cm^2 for glucose electrooxidation compared to that of other PdIn/HAps. The relatively low specific activities of Pd$_{70}$In$_{30}$/HAp and Pd$_{50}$In$_{50}$/HAp (1.09 and 1.02 mA/cm^2) are due to the oxidation of carbonaceous compounds at a potential of about 0 V. With the addition of In, the onset potential of Pd-based catalysts shifted to
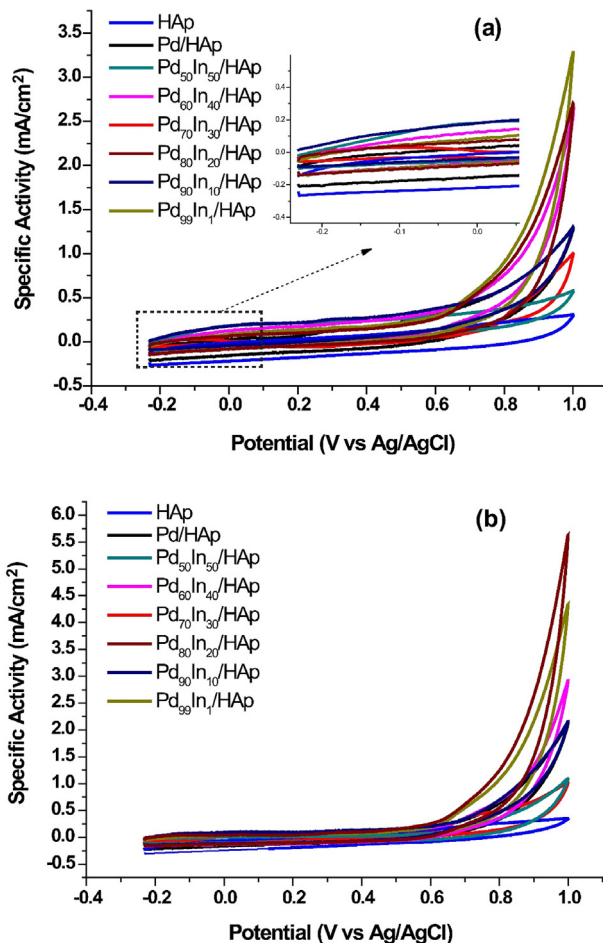

Fig. 7 – CV curves of PdIn/HAp catalysts in a) 1 M KOH and b) 1 M KOH + 0.5 M Glucose.

negative potentials compared to that of Pd/HAp, indicating that the poisoning severity of PdIn alloy catalysts for glucose electrooxidation decreased due to the synergism between Pd and In Ref. [78].

Electrochemical stability

Chronoamperometric curves of HAp, Pd/HAp, and Pd$_{80}$In$_{20}$/HAp in 1 M KOH + 0.5 M Glucose solution at a scan rate of 50 mV/s were given in Fig. 8. The current density of the Pd$_{80}$In$_{20}$/HAp catalyst dropped sharply from 2.76 mA/cm^2 to 1.96 mA/cm^2 in the first 25 s. The initial current drop in the first 25 s for HAp and Pd/HAp were found to be 2.29 and 1.14 mA/cm^2, respectively, and the sharp decrease in current density was assigned to carbonaceous compounds deposited on the catalyst surface. The percentage current loss after 1000 s for HAp, Pd/HAp, and Pd$_{80}$In$_{20}$/HAp was determined as 94.9%, 62.6%, and 49.6, respectively. From Fig. 8b, it is clear that the Pd$_{80}$In$_{20}$/HAp catalyst has the longest stability for 1000 s compared to these of Pd/HAp and HAp. As shown in Figure S3, the glucose diffusion coefficient for HAp, Pd/HAp, and Pd$_{80}$In$_{20}$/HAp were determined with the slope of the linear plot of I vs. t$^{−1/2}$. Cottrell equation was used to obtain the diffusion coefficient of the glucose:

Table 2 – Electrochemical performance of PdIn/HAps.

Catalysts	Specific Activity in 1 M KOH	Onset Potential in 1 M KOH+ 0.5 M Glucose	Specific Activity in 1 M KOH + 0.5 M Glucose
HAp	0.31	–	0.35
In/HAp	0.46	0.35	0.83
Pd/HAp	1.28	0.75	2.12
$Pd_{50}In_{50}$/HAp	0.58	0.67	1.02
$Pd_{60}In_{40}$/HAp	2.59	0.65	2.92
$Pd_{70}In_{30}$/HAp	1.00	0.69	1.09
$Pd_{80}In_{20}$/HAp	3.28	0.62	5.64
$Pd_{90}In_{10}$/HAp	1.30	0.67	2.16
$Pd_{99}In_{1}$/HAp	2.70	0.63	4.34

$$i(t) = \frac{nFACD^{1/2}}{t^{1/2}\pi^{\frac{1}{2}}} = Kt^{-1/2} \qquad (4)$$

where C, D, and A represent the concentration of glucose, diffusion coefficient, and real surface area. Diffusion coefficient of the glucose for HAp/GCE, Pd/HAp/GCE, and PdIn/HAp/GCE was calculated to be 7.81×10^{-10}, 1.29×10^{-9}, and 5.94×10^{-10} cm^2 s^{-1}, respectively.

Impedance patterns for glucose electrooxidation
Fig. 9a shows the EIS profiles of $Pd_{80}In_{20}$/HAp, Pd/HAp, and HAp materials in 1 M KOH + 0.5 M Glucose solution at 1 V

potential. The decrease in the diameter of the EIS curves indicates decreased charge transfer resistance and increased electrocatalytic activity. Accordingly, $Pd_{80}In_{20}$/HAp showed higher electrocatalytic activity for glucose electrooxidation than other catalysts, and the EIS results are in harmony with the CV and CA results. Electrochemical tests show that $Pd_{80}In_{20}$/HAp has higher specific activity and stability for glucose electrooxidation than other anode catalysts. The performance of $Pd_{80}In_{20}$/HAp is attributed to the alteration of its electronic properties by modifying the surface of Pd with In and the optimum value of the distance between the Fermi level and the d band center of Pd. The fitted EIS profile of the $Pd_{80}In_{20}$/HAp was shown in Fig. 9b. R, W, and Q in the equivalent resistance model represent the resistance, Warburg element, and the constant phase element, respectively. Obtaining good fitting shows that the electrooxidation process on $Pd_{80}In_{20}$/HAp could be sensibly explained by the proposed equivalent circle model. In the proposed model, R1 and R2 are attributed to the resistance of the solution, while R3 of 3.380 Ω cm^2 represents the charge transfer resistance.

The effect of scan rates on the electrooxidation of $Pd_{80}In_{20}$/HAp catalyst in 1 M KOH and 0.5 M Glucose solution is shown in Fig. 10a. It was determined from Fig. 10a that the peak current for glucose electrooxidation increased as the scan rates increased. Fig. 10b shows a linear relationship between scan rates and peak current for glucose electrooxidation on PdIn/HAp, indicating glucose is transported from the bulk
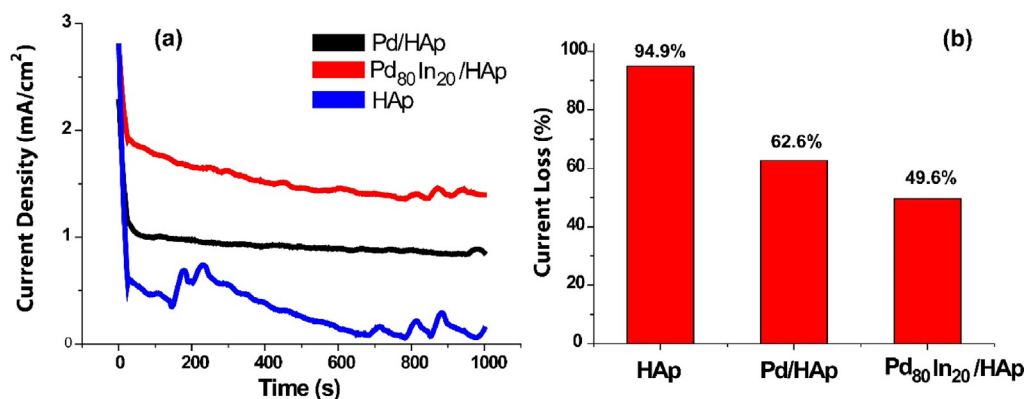

Fig. 8 – a) Chronoamperometric curves and b) current loss after 1000 s for $Pd_{80}In_{20}$/HAp in 1 M KOH+ 0.5 M Glucose.
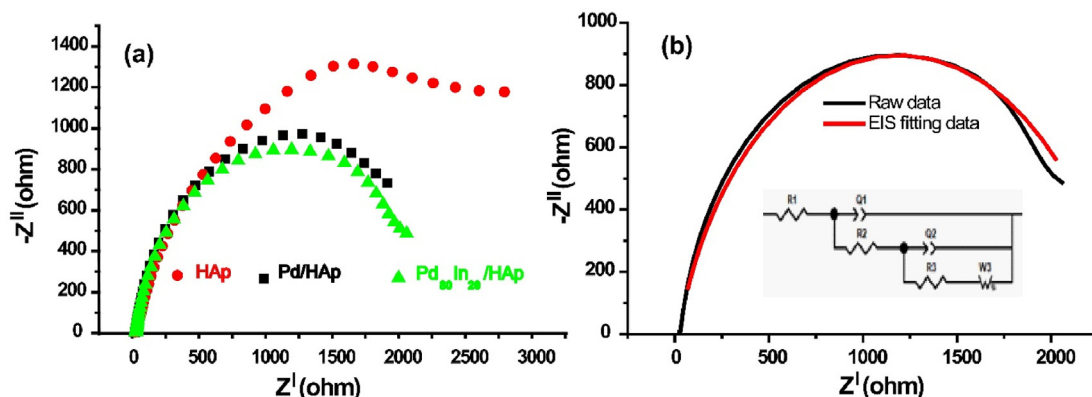

Fig. 9 – a) EIS profiles of PdIn/HAp, Pd/HAp, and HAp, and b) equivalent circuit model for $Pd_{80}In_{20}$/HAp for glucose electrooxidation.
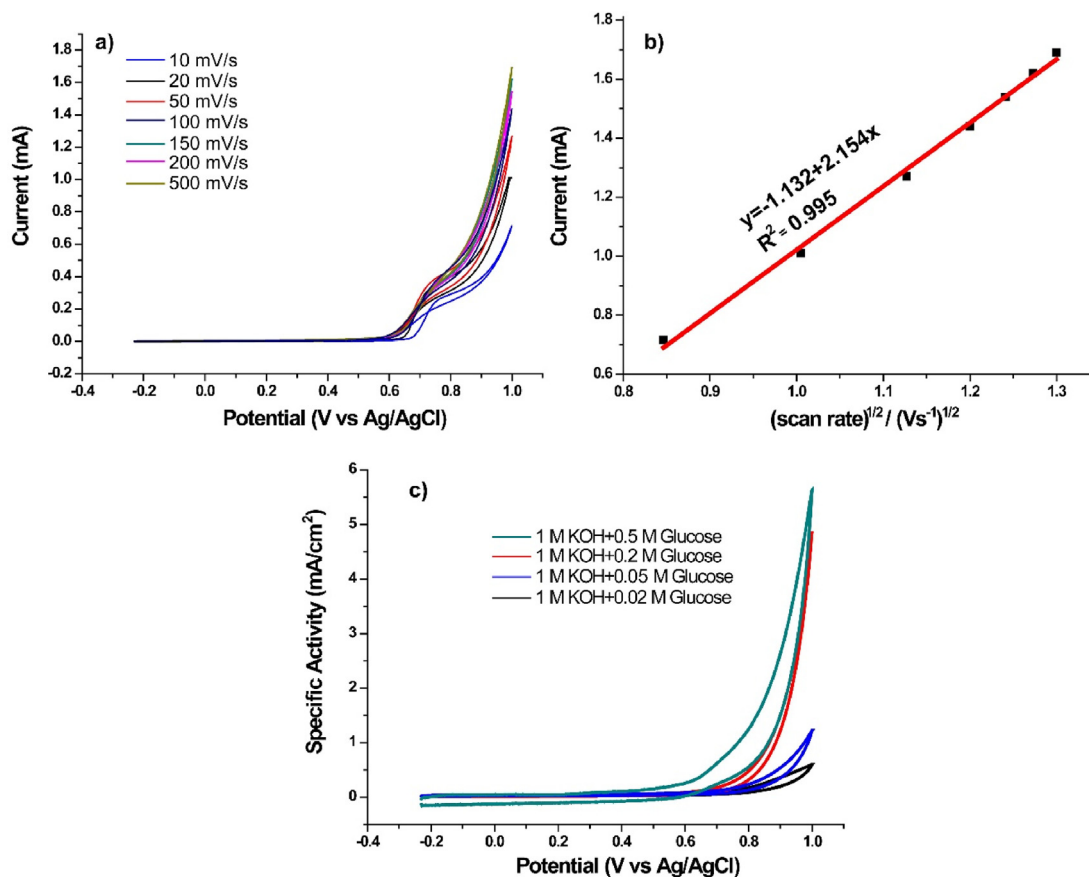
Fig. 10 — (a) CV of the PdIn/HAp in 1 M KOH + 0.5 M glucose at varying scan rates, (b) current vs. (scan rate)$^{1/2}$, and (c) 1 M KOH + 0.02–0.5 M glucose.

solution to the PdIn/HAp modified GCE surface predominantly by mass transfer [29]. The effect of glucose concentration on glucose electrooxidation with $Pd_{80}In_{20}$/HAp is shown in Fig. 10c. The specific activities were determined as 0.60, 1.22, 4.87 and 5.64 mA/cm^2 for 0.02, 0.05, 0.2 and 0.5 M glucose concentrations in 1 M KOH solution, respectively. The

increase in specific activity with increasing glucose concentration was attributed to the presence of sufficient OH$^-$ group adsorption on active sites of PdIn/HAp [79].

In the literature, the activities of various materials toward the glucose electrooxidation reaction were generally reported for sensor applications. There is limited literature on the fuel

Table 3 — Literature on anode catalyst for glucose electrooxidation.

Anode catalyst	Solution ($C_{KOH \text{ or } NaOH}$/Glucose)	Scan rate (mV/s)	Specific activity (mA/cm^2)	Mass activity (mA/mg)	Onset potential (V)	References
Pt/Pd/p-1,8-DAN	0.10 M/0.025 M	50	0.051	—	−0.28	[80]
AgPt@C	1 M/5 mM	50	0.025	—	0.15	[81]
Pd−Ce$_2$O$_3$/ITO	0.5 M/0.5 M	50	8.125	—	0.101	[82]
Mg$_{65}$Bi$_{35}$	0.5 M/0.5 M	50	8.04	125	0.513	[43]
Benzothiophene derivative	1 M/0.5 M	50	0.729	3.345	−0.19	[83]
Pd$_{90}$In$_{10}$/CNT	1 M/0.5 M	50	0.98	161.15	−0.319	[52]
N doped-G/ITO	1 M/0.5 M	50	9.12	—	−0.22	[84]
Pd$_3$Cu−B/C	0.1 M/0.5 M	100	—	105	—	[29]
Graphene/Ni−Fe	0.2 M/0.01 M	50	ca. 0.5	—	0.3	[50]
G/ITO	1 M/0.5 M	50	6.58	—	−0.24	[69]
Pt−Ni−Cu/GCE	0.1 M/0.01 M	100	0.96	—	ca −0.5	[51]
Indole-based organic catalyst	1 M/0.5 M	50	0.52	2.45	0.57	[85]
CoO$_x$@CNF	0.1 M/0.05 M	50	ca 6	—	—	[86]
Ru/CNT	1 M/0.5 M	50	1.86	160.6	—	[38]
Ni−Cu/GC	0.5 M/0.05 M	100	—	409	ca 0.2	[45]
Pd$_{80}$In$_{20}$/HAp	1 M + 0.5 M	50	5.64	159.4	0.62	In this study

cell, which requires electrochemical measurements with higher glucose and supporting electrolyte concentrations compared to sensor applications. The electrochemical performances of the materials prepared as anode catalysts for DGFCs in recent years were summarized in Table 3. Elkholy et al. reported the specific activity for glucose electrooxidation on $Pd-Ce_2O_3$/ITO as 8.125 mA/cm^2 and emphasized that Ce_2O_3 had a lowering effect on the charge transfer resistance [82]. On the other hand, Shi et al. reported the specific activity of $Mg-Bi$ alloy catalyst as 8.04 mA/cm^2 under similar conditions [43]. In our study, the specific activity of glucose electrooxidation with $Pd_{80}In_{20}$/HAp electrocatalyst was found to be 5.64 mA/cm^2. The specific activity of $Pd_{80}In_{20}$/HAp for glucose electrooxidation can compete with the activity values obtained under similar conditions in the literature. Er et al., reported the specific activity of CNT-supported PdIn alloy catalyst for glucose electrooxidation as 0.98 mA/cm^2 [52]. The electrocatalytic performance of $Pd_{80}In_{20}$/HAp catalyst is 5.8 times higher than $Pd_{90}In_{10}$/CNT, indicating that HAp could be a good alternative to CNT. The positive contribution of HAp to the electrocatalytic activity is attributed to the fact that Ca and phosphate in its structure create isolated Pd regions and enable the third-body effect [87]. In addition, it was concluded that the hydroxyl-rich structure of HAp caused the separation of CO species from the catalyst surface and increased the electrocatalytic activity for glucose electrooxidation by bifunctional effect.

Conclusions

PdIn/HAps were successfully synthesized by precipitation and $NaBH_4$ reduction method toward glucose electrooxidation. The morphological and chemical structure of PdIn/HAp were investigated by using TEM, XRD, and ICP-MS. The average particle size and crystal size of the PdIn nanoparticles are found to be 9.18 nm and 6.81 nm, respectively. Among the PdIn/HAps at different metal compositions, the $Pd_{80}In_{20}$/HAp catalyst exhibited the highest electrocatalytic activity for glucose electrooxidation with a specific activity of 5.64 mA/cm^2. The percentage current loss after 1000 s for HAp, Pd/HAp, and $Pd_{80}In_{20}$/HAp was determined as 94.9%, 62.6%, and 49.6, respectively. The $Pd_{80}In_{20}$/HAp catalyst has long-term stability at higher activity than Pd/HAp and HAp. The charge transfer resistance of the $Pd_{80}In_{20}$/HAp catalyst was found to be 3380 Ω/cm^2. The charge transfer resistance of $Pd_{80}In_{20}$/HAp is lower than HAp and Pd/HAp. Thanks to the hydroxyl ions in the HAp structure, increases the CO tolerance of the catalyst system. It is predicted that HAp will be used more widely as a catalyst support material, as it reduces the severity of CO poisoning, which is an important handicap for the oxidation of carbon-containing fuels namely glucose, ethylene glycol, formic acid, methanol, and ethanol.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2022.06.314.

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