Porous 3D Inorganic Superstructure of Pd–Ir Aerogel as Advanced Support-Less Anode Electrocatalyst toward Ethanol Oxidation

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ABSTRACT: For the first time, synthesis of Pd–Ir aerogel is reported in this manuscript. The Pd–Ir aerogel is synthesized using the controlled assembly of nanoparticles (NPs) (Ir and Pd) during the facile, surfactant-free, fast, and one-step gelation process in an aqueous environment followed by CO₂ supercritical drying. In this process, no chemical reagents are employed to induce the gelation, and change of temperature is employed to create anisotropic electrostatic repulsions between NPs. In addition, the kinetics and type of product are controlled by the change of temperature. The Pd–Ir aerogel shows a three-dimensional (3D) architecture with a very high porosity and an ultralow density (0.016 g cm⁻³). The Pd–Ir aerogel is applied as an advanced 3D electrocatalyst for the ethanol oxidation reaction (EOR) and offers a remarkable electrocatalytic efficiency (5416.1 mA mg⁻¹ Pd) in a basic environment. The exceptional electrocatalytic activity and stability of the resultant aerogel are attributed to two crucial reasons: (1) unique structure of Pd–Ir aerogel and (2) synergistic effect of Ir element. Micro- and mesopore characteristics provide a large surface area, while macropore characteristic guarantees accessibility to active sites. Furthermore, the self-supporting character of the Pd–Ir aerogel may hinder the degradation of durability observed in carbon-based electrocatalysts due to corrosion of carbonaceous support. Moreover, the Ir element as a co-metal in the structure of Pd–Ir aerogel acts as a very efficient promotor in the EOR and can change the electronic structure of Pd, which facilitates the electrooxidation of EtOH in alkaline media.

INTRODUCTION

Utilization of fossil fuels has created fundamental problems (e.g., environmental pollution, greenhouse gas emission, etc.). It is proved that direct liquid fuel cells (DLFCs) such as direct ethanol fuel cells (DEFCs) are proper alternatives to fossil fuels on account of their widespread advantages (e.g., safe storage, high energy density, security, etc.). However, commercialization of DEFCs still faces two vital obstacles such as unfavorable durability and inadequate efficiency of catalysts. Therefore, finding suitable catalysts for electrocatalysis has emerged as a hot topic in the field of materials science. Scientists have dedicated their effort to develop new routes for the development of materials science. Numerous studies on unique architectures in materials science have led to the growth and substantial progress in this field. In the past few years, apparition of self-assembly has created a revolutionary in nanoscience. Self-assembly is a usual bottom-up approach to obtain well-defined complex architectures. In this process (self-assembly), nanoparticles (NPs) act as building blocks for the creation of unique architectures. Likewise, the assembly of NPs into functional architectures is of special relevance for realistic development, and it represents a rapidly growing branch of research. Scientists have synthesized a variety of unique architectures by utilizing the self-assembly strategy. Among them, noble-metal aerogels (NMAs) have recently appeared as a unique class of porous inorganic superstructures.

As a unique and novel kind of inorganic superstructures, NMAs have shown extraordinary characteristics (e.g., large porosity, high surface area, lightweight, etc.). They are created during the controlled growth of NPs in three orientations of x, y, and z axes to make three-dimensional (3D) architectures. Compared to one-dimensional (1D) and two-dimensional (2D) architectures, NMAs offer unique physicochemical characteristics. These inorganic modern polymers have shown exceptional advantages of metals and can retain the intrinsic characterizations of common aerogels. Inorganic superstructures provide support-less and macroporous characteristics. The support-less property of NMAs may hinder the decadence of durability observed in metal NPs decorated on carbon support owing to corrosion. Moreover, facile access to active sites has been guaranteed by the macroporous characteristic of NMAs. To resolve the above-mentioned challenges for DEFCs, NMAs are promising
nanomaterials owing to their self-supporting and macroporous characteristics.

A strategy for the production of NMAs was reported for the first time by Eychmüller and co-workers, who explained the controlled organization of NPs in aqueous media to create mono- and bimetallic hydrogels.11 After Eychmüller and co-workers, many researchers tended to the chemistry of NMAs. Hence, many attempts have been devoted to develop this field. Gelation step is a very vital stage in the production of NMAs since 3D architectures are formed in this stage. Therefore, all attempts were accomplished for the facilitation of this stage (gelation stage). Commonly, two strategies were utilized to create NMAs: (1) in situ reduction and subsequent fusion and (2) self-assembly. The first strategy involves in situ reduction of NPs and subsequent linkage of the NPs by employing a strong reducing reagent in an aqueous medium. For the second strategy, metallic NPs (such as Ag, Pd, Pt, and Au) are first created in the presence of a stabilizer. The colloidal suspension was then concentrated, and the gelation can be induced via addition of a destabilizer (e.g., dopamine, calcium carbonate, sodium carbonate, hydrogen peroxide, etc.). The advantage of the first strategy over the second approach lies in the fact that gelation is remarkably simplified since the concentration stage can be avoided. 3D gels were dried by employing supercritical drying with liquid carbon dioxide, and 3D aerogels were obtained. For both strategies, the creation mechanism of NMAs has been unclear to date since formation of 3D gel is a highly complex process. Production of mono- and binary NMAs have been reported in the literature. Monometallic Pd aerogel synthesized in the presence of TOPO was reported by Zareie and colleagues.7 They applied these 3D superstructures for electrooxidation of EtOH in a basic environment. Production of platinum nanospheres and nanocube aerogels in the presence of hydrazine monohydrate was reported in the literature.12 Liu and colleagues reported that self-assembly of nanowires with nanotube geometry leads to the creation of bimetallic PtAg nanotubular aerogels (PtAg NTAGs).10 These bimetallic NMAs show a high efficiency toward oxidation of formic acid (FA). In recent years, many attempts have been made to facilitate the gelation process for the creation of NMAs. However, synthesizing NMAs still faces several obstacles such as utilization of a surfactant and multistep strategies.

Synthesis of the Pd–Ir aerogel is reported for the first time in this manuscript. The Pd–Ir aerogel was synthesized during the controlled assembly of both NPs (Ir and Pd) during the surfactant-free, fast, and one-step gelation process in aqueous environment followed by CO2 supercritical drying. Reduction of Pd2+ and Ir3+ ions was carried out in the presence of sodium borohydride without any surfactant. In this process, no chemical compound is employed to induce gelation, and temperature change was employed to create anisotropic electrostatic repulsions between building blocks. The Pd–Ir aerogel was applied as an advanced 3D electrocatalyst for the ethanol oxidation reaction (EOR), and it showed remarkable electrocatalytic activity and durability in alkaline media. Scheme 1 displays the production process of the Pd–Ir aerogel and its application toward the EOR.

# RESULTS AND DISCUSSION

It is well corroborated that the shape engineering of Pd-based nanostructures and combination of co-metals with Pd can effectively enhance the electrocatalytic activity of a catalyst. The Pd–Ir aerogel was synthesized by reducing Pd2+ and Ir3+ ions in the presence of sodium borohydride followed by CO2 supercritical drying. Controlled assembly of both NPs (Ir and Pd) during the surfactant-free, fast, and one-step gelation process in an aqueous environment is carried out for the creation of a 3D Pd–Ir hydrogel. Reduction of Pd2+ and Ir3+ ions with sodium borohydride leads to the creation of a colloidal suspension. Scientists corroborated that gelation occurs in the presence of a destabilizing agent (e.g., dopamine, calcium carbonate, sodium carbonate, hydrogen peroxide, etc.) to overcome the isotropic electrostatic repulsions between NPs. In the present work, temperature was employed as an effective destabilizing agent for the transportation of isotropic electrostatic repulsions between the NPs into anisotropic forms, leading to the assembly of NPs to form the Pd–Ir hydrogel. Moreover, the kinetics and the type of product are controlled by the change of temperature. Table 1 shows the effect of temperature on the gelation process. As shown, gelation does not occur at temperatures of 25 and 30 °C, and Pd–Ir NPs are achieved since at these temperatures, the energy needed to overcome the electrostatic repulsions between the NPs is not supplied. As shown, temperatures of 40, 50, 60, and 65 °C supply the required energy to create anisotropic electrostatic repulsions and linkage of NPs. Based on Table 1, the optimum temperature for the creation of Pd–Ir hydrogel is 60 °C. The Pd–Ir hydrogel can produce various products depending on the type of drying. Drying the Pd–Ir hydrogel at ambient temperature collapses the 3D architecture due to the capillary pressure and leads to the creation of a Pd–Ir aerogel. Utilization of the freeze-drying process to remove the liquid produces damage to the 3D hydrogel architecture owing to the formation of solvent crystal and leads to the creation of a Pd–Ir cryogel. To retain the porosity and 3D network of the Pd–Ir hydrogel, CO2 supercritical drying was applied and a Pd–Ir aerogel was obtained. Utilization of supercritical drying is vital to maintain the 3D hydrogel network because no crystallization or capillary forces will occur. Therefore, the Pd–Ir hydrogel during the CO2 supercritical drying was transformed to the Pd–Ir aerogel. Figure 1 clarifies a monolithic network with an ultralow density (0.016 g cm–3) of Pd–Ir aerogel. Figure 1A shows a monolith Pd–Ir hydrogel synthesized in a glassy vial at a temperature of 60 °C. Figure 1B exhibits the Pd–Ir aerogel balanced on dandelion, which corroborates the ultralow density of the Pd–Ir aerogel.

Both field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were utilized to study the 3D architecture with a very high porosity of Pd–Ir aerogel. Figure 2A–B shows the FESEM micrographs recorded...
Figure 1. Photographs of (A) Pd–Ir hydrogel and (B) Pd–Ir aerogel balanced on the dandelion (pictures were taken by the authors. Copyright 2020).

Figure 2. FESEM micrographs corresponding to the Pd–Ir aerogel (A–B), TEM (C), and HR-TEM (D) micrographs corresponding to the Pd–Ir aerogel.

Figure 3. XRD pattern of Pd–Ir aerogel.

Figure 4. Nitrogen isotherm of the Pd–Ir aerogel showing a surface area of 42.1 m² g⁻¹. The inset shows the pore size distribution of the Pd–Ir aerogel via the BJH model.

at 500 nm and 1 μm for the Pd–Ir aerogel. Extended nanochains for the production of a 3D network are well corroborated by these micrographs. As mentioned in the Introduction section, NMAs are inorganic superstructures with a large porosity, and the FESEM micrographs clarify the very high porosity and tunnels for the Pd–Ir aerogel. In addition, Figure 2C displays the TEM micrograph related to the Pd–Ir aerogel. Linkage of NPs for the fabrication of a huge 3D nanonetwork is depicted by this image. Moreover, this micrograph well confirmed the many open pores as well as expanded nanochains of the resultant aerogel. Moreover, the high-resolution TEM (HR-TEM) image was acquired to identify the structure of the Pd–Ir aerogel. Figure 2D reveals the HR-TEM image related to the Pd–Ir aerogel. As represented, this micrograph exhibits interplanar spacings of 0.225 and 0.22 nm, which can be assigned to the Pd(111) and Ir(111) planes, respectively. The FESEM, TEM, and HR-TEM micrographs are completely corroborated the production of the 3D architecture of the Pd–Ir aerogel with many open pores and tunnels.

X-ray diffraction (XRD) was conducted to investigate the crystallinity and bulk compounds of the Pd–Ir aerogel. XRD data were collected at angles of 30°–90° (Figure 3). In this pattern, the advent of five distinct peaks at 40.23, 46.80, 68.34, 82.39, and 86.93° corroborates the presence of Pd in the structure of the Pd–Ir aerogel according to the face-centered cubic (FCC) crystal structure of Pd (PDF #87-0638). Likewise, the advent of reflection peaks at angles of 40.01, 46.53, 67.92, 81.85, and 86.34° confirms the presence of Ir in the structure of resultant aerogel in accordance with the FCC crystal structure of Ir (PDF #88-2342). In addition, the diffraction peaks of the Pd–Ir aerogel showed a slight shift in comparison to the standard Pd (PDF #87-0645), which confirms the generation of alloy nanostructure. As shown in the XRD pattern, the intensity of the (111) phase is larger in comparison to the (200), (220), (311), and (222) phases. It is corroborated that the (111) phase of Pd is less prone to oxidation; therefore, this phase is proper for fuel cell application.¹

To reveal the chemical compositions of the Pd–Ir aerogel, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out, which confirmed that the Pd (with a percentage of 87.4 wt %) and Ir (with a percentage of 12.6 wt %) elements constitute the Pd–Ir aerogel. Both ICP-AES and XRD analyses well confirmed the crystalline phases and chemical compounds of the Pd–Ir aerogel.

The surface area and porosity of the Pd–Ir aerogel have been investigated by the N₂ isotherm analysis. Figure 4 shows the adsorption/desorption isotherm of N₂ on the surface of the Pd–Ir aerogel. The N₂ isotherm recorded for the Pd–Ir aerogel clari...
promising support-less electrocatalyst for electrocatalysis applications.

Figure 5A shows the cyclic voltammetry (CV) curves recorded in a 1.0 M KOH solution for Pd–Ir aerogel, Pd aerogel, and Pd/C at room temperature (RT) with a sweep rate of 20.0 mV s\(^{-1}\). Oxidation of Pd surface and desorption of hydrogen peaks are created for each catalyst in forward sweep in the potential regions of (0.2–0.5 V) and (−1.0 to −0.6 V), respectively. The advent of peaks (at −1.0 to −0.6 V) in backward sweep for each sample is related to the adsorption of hydrogen on the surface of three catalysts. The electrochemical active surface area (ECSA) is a reliable index for the assumption of active sites related to each catalyst. This index (ECSA) was assessed by integrating columbic charge related to the reduction peaks of PdO, which are located in backward sweep in the potential range of −0.4 to −0.2 V for all catalysts. The Pd–Ir aerogel, Pd aerogel, and Pd/C show ECSA values of 67.8, 38.9, and 10.06 m\(^2\) g\(^{-1}\), respectively. This parameter can predict the electrocatalytic activity of a catalyst, and the greater value of ECSA is further corroborated by the greater adsorption/desorption of hydrogen peaks on the surface of the Pd–Ir aerogel.

The electrocatalytic performance of Pd–Ir aerogel, Pd aerogel, and Pd/C catalysts was recorded in 1.0 M KOH containing 0.5 M EtOH solution under ambient conditions. The responses of working electrodes covered by the Pd–Ir aerogel, Pd aerogel, and Pd/C toward the EOR are shown in Figure 5B. Profiles corresponding to each modified electrode in anodic sweep reflect a strong peak, which are attributed to the electrooxidation reaction of EtOH onto the surface of three electrodes. However, it is corroborated that the electrooxidation reaction of EtOH is accompanied by the creation of intermediate species. Hence, in each profile, a strong peak in the backward sweeps appears on account of the oxidation of residue intermediates. As a result, a greater ratio of current density in forward sweep to the current density in backward sweep (\(J_f/J_b\)) is a reliable factor to evaluate the strong and poisoning of an electrocatalyst during the electrooxidation process of EtOH.\(^{1−5}\) Tolerance to poisoning of the Pd–Ir aerogel (1.45) is superior to those of the Pd aerogel (1.43) and Pd/C (0.6).

Comparison of the three profiles depicted that the Pd–Ir aerogel, Pd aerogel, and Pd/C show mass activities of 5416.1, 4118.8, and 1007.9 mA mg\(\text{Pd}\)\(^{-1}\), respectively. Moreover, the Pd–Ir aerogel (−522 mV) shows a negative shift in onset potential compared to the Pd aerogel (−498 mV) and Pd/C (−460 mV), corroborating higher kinetics of the EOR for the Pd–Ir aerogel. Moreover, the peak potential of the Pd–Ir aerogel (−0.04 V) was slightly located at more negative potential in comparison to the Pd aerogel (−0.026 V), which means that the EtOH molecules are easily oxidized on the surface of the Pd–Ir aerogel. In addition, the Pd aerogel shows a superior electrocatalytic activity compared to Pd/C due to the unique structural characteristics. Based on the observations, it is well corroborated that the electrooxidation of EtOH on the Pd–Ir aerogel clarifies remarkable electrocatalytic activity due to the synergistic effect of Ir and the unique structural characteristics of the Pd–Ir aerogel. In addition, Table 2 presents the mass activity values of Pd-based nanostructures toward the EOR. 1D, 2D, and 3D self-supported Pd-based nanostructures were selected to compare the electrocatalytic activities for electrooxidation of ethanol. As shown, the Pd–Ir aerogel and the Pd aerogel display superior electrocatalytic activity toward the EOR despite the lower EtOH concentration as well as sweep rate.

It is well corroborated that the change of temperature severely affects the electrocatalytic activity of a catalyst. Hence, to realize the effect of temperature on the performance of Pd–Ir aerogel, linear sweep voltammetry (LSV) was conducted at temperatures of 25, 30, 35, and 45 °C. Figure 6A–C shows the profiles of LSV

Table 2. Comparison of Mass Activities of 1D, 2D, and 3D Self-Supported Pd-Based Nanostructures toward Ethanol Oxidation in Alkaline Media

| catalyst          | electrolyte concentration (M) | ethanol concentration (M) | scan rate (mV s\(^{-1}\)) | current density (mA mg\(\text{Pd}\)\(^{-1}\)) | ref |
|-------------------|-------------------------------|---------------------------|---------------------------|-----------------------------------------------|-----|
| Pd\(_{2}\)Ag\(_{1}\) single nanowires | 1.0                           | 1.0                       | 50.0                      | 3472.0                                        | 35  |
| Pd nanosheets     | 1.0                           | 1.0                       | 50.0                      | 3472.0                                        | 35  |
| 3D PdCu nanosheets| 1.0                           | 1.0                       | 50.0                      | 3472.0                                        | 35  |
| PdSn nanosheets dendrites | 1.0                           | 1.0                       | 50.0                      | 3472.0                                        | 35  |
| 2D Pd–Ag nanodendrites | 1.0                           | 1.0                       | 50.0                      | 3472.0                                        | 35  |
| Pd nanodendrites  | 1.0                           | 1.0                       | 50.0                      | 3472.0                                        | 35  |
| Pd aerogel        | 1.0                           | 0.5                       | 20.0                      | 4118.8                                        | this work |
| Pd–Ir aerogel     | 1.0                           | 0.5                       | 20.0                      | 4118.8                                        | this work |
corresponding to each catalyst (Pd/C, Pd aerogel, and Pd–Ir aerogel) in 0.5 M EtOH at basic media. Each profile showed that the electrocatalytic performance of all catalysts is promoted by boosting the temperature. Activation energy ($E_a$) was calculated by utilizing the value of specific activity at each temperature for a given potential ($-0.1$ V) (Figure 6D–F) according to the Arrhenius relationship eq 1:

$$I = A e^{-E_a/R T}$$

where $E_a$, $I$, and $T$ refer to the activation energy, temperature (K), and specific activity at a given potential ($-0.1$ V), and $R$ denotes the gas constant. Activation energies calculated for Pd–Ir aerogel (5.89 kJ mol$^{-1}$), Pd aerogel (11.2 kJ mol$^{-1}$), and Pd/C (22.1 kJ mol$^{-1}$) corroborate lower $E_a$ and higher kinetics of electron transport on the Pd–Ir aerogel surface.

CV at sweep rates of 10.0, 20.0, 30.0, and 40.0 mV s$^{-1}$ was recorded in 1.0 M KOH containing 0.5 M EtOH on the working electrode covered by the Pd–Ir aerogel to assess the mass transport process. Response of the Pd–Ir aerogel toward the EOR at different sweep rates is illustrated in Figure 7A. Profiles confirmed that the specific activity of the Pd–Ir aerogel is enhanced by boosting the sweep rate. A proper linear relationship is represented in Figure 7B, which supposes that the electrooxidation process of EtOH on the Pd–Ir aerogel may be controlled by mass transport.$^{19-24}$

As mentioned above, inadequate durability of catalysts is one of the crucial challenges in commercialization of DEFCs. The chronoamperometry (CA) technique was utilized as a proper analysis to distinguish the durability of an electrocatalyst. Electrooxidation of EtOH at a constant potential of $-0.2$ V was conducted on the working electrodes covered by the Pd–Ir aerogel, Pd aerogel, and Pd/C at 298 K, and the CA curves are shown in Figure 7C. Decomposition of EtOH on the surface of all modified electrodes leads to high specific activities for catalysts at the initial step of CA evaluations. High specific activity at early step of CA is ascribed to the clean available active sites for each catalyst. Fast decadence of specific activity related to three electrocatalysts implies severe poisoning of active sites during the EOR.$^{25-30}$ The calculated value of $J_{0s}/J_s$ of the CA profile was utilized to study the decay kinetics of a catalyst.$^{28-34}$

Figure 6. LSV profiles recorded at various temperatures for (A) Pd–Ir aerogel, (B) Pd aerogel, and (C) Pd/C. Arrhenius plots for (D) Pd–Ir aerogel, (E) Pd aerogel, and (F) Pd/C at $-0.1$ V.

Figure 7. CV profiles recorded at various scan rates toward EtOH on the Pd–Ir aerogel (A); plot of forward peak density vs square root of the scan rate (B); profiles of chronoamperometry (CA) related to Pd/C, Pd aerogel, and Pd–Ir aerogel for 7200s (vs Hg/HgO) at a potential of $-0.2$ V (C); and the mass activity recorded for three electrocatalysts versus cycle number in 1.0 M KOH + 0.5 M EtOH with a scan rate of 20.0 mV s$^{-1}$ (D).
Calculation of this ratio for Pd–Ir aerogel (0.81), Pd aerogel (0.53), and Pd/C (0.46) catalysts corroborates the lower decay of specific activity profile corresponding to the Pd–Ir aerogel in comparison to the other catalysts. The cycling durabilities of the Pd–Ir aerogel, Pd aerogel, and Pd/C electrocatalysts for the electrooxidation of EtOH were acquired for 500 cycles in the 1.0 M KOH containing 0.5 M EtOH with a scan rate of 20 mV s⁻¹.

The mass activity values for all electrocatalysts were recorded after all 50 cycles, and the mass activity values are shown in Figure 7D. As reflected, the mass activities of the Pd–Ir aerogel, Pd aerogel, and Pd/C for electrooxidation of EtOH after 500 cycles are 71.7, 52.1, and 27.9%, respectively, which indicates the superior electrochemical efficiency and durability of the Pd–Ir aerogel toward the EOR compared to the other catalysts. In addition, the FESEM image of the Pd–Ir aerogel after CA experiment was used to confirm the better stability of the Pd–Ir aerogel. Figure 8 shows the FESEM micrograph related to the Pd–Ir aerogel after CA experiment. Comparison of morphologies of the Pd–Ir aerogel before and after CA test showed that the morphology of the Pd–Ir aerogel is slightly changed after CA test, which confirms its excellent electrochemical stability.

To further study the electrocatalytic activity of both NMAs, the Pd–Ir aerogel and Pd aerogel were utilized as anode components in direct ethanol fuel cells (DEFCs). The performances of Pd-based nanomaterials in DEFCs were usually investigated at high operating temperatures (70–150 °C). However, the efficiencies of the Pd–Ir aerogel and Pd aerogel were evaluated as anode nanomaterials in DEFCs at RT (25 °C). Figure 9 clarifies the polarization profiles of both NMAs and Pd/C catalysts. When Pd/C was utilized as the anode catalyst in DEFC at RT (25 °C), the open-circuit voltage (OCV) was 0.64 V, while the maximum current density (MCD) and maximum power density (MPD) were 80.8 mA cm⁻² and 13.81 mW cm⁻², respectively. Based on the recorded profiles in Figure 9, both aerogels show better electrocatalytic activity in DEFCs compared to the Pd/C catalyst. As shown, the value of OCV for the Pd–Ir aerogel is 0.93 V, which is higher in comparison to the Pd aerogel (0.86) and Pd/C (0.64 V), suggesting that the Pd–Ir aerogel was less poisoned by adsorbed species from ethanol compared to other catalysts. Moreover, the Pd–Ir aerogel not only exhibits a higher MCD (106.9 vs 85.8 mA cm⁻²) but also offers a higher MPD (23.4 vs 19.4 mW cm⁻²) in comparison to Pd aerogel. Undoubtedly, the Pd–Ir aerogel can be employed as an advanced support-less anode catalyst in DEFCs.

Decomposition of EtOH on the Pd–Ir aerogel confirms remarkable electrocatalytic activity and durability due to the synergistic effect of Ir and the unique structural characteristics of Pd–Ir aerogel. The 3D architecture of the Pd–Ir aerogel with a very high porosity reflects both support-less and macroporous characteristics. Prevention from degradation of stability and facile access to the active sites for reactant molecules have been guaranteed by the support-less and macroporous characteristics of the Pd–Ir aerogel, respectively. Moreover, the Ir element, as a co-metal in the structure of the Pd–Ir aerogel, acts as a very efficient promoter for the electrooxidation reaction of EtOH and can change the electronic structure of Pd, which facilitates the EOR in alkaline media.

**CONCLUSIONS**

For the first time, the 3D architecture of the Pd–Ir aerogel was created using the controlled assembly of both NPs (Ir and Pd) during the surfactant-free, fast, and one-step gelation process in an aqueous environment followed by CO₂ supercritical drying. In this process, change of temperature was employed to create the anisotropic electrostatic repulsions between building blocks. The kinetics and the type of product are controlled by the change of temperature. The Pd–Ir aerogel clarifies a monolith 3D architecture with very high porosity and lightweight (0.016 g cm⁻³). The Pd–Ir aerogel was applied as an advanced 3D electrocatalyst for EtOH oxidation, and it reflected the remarkable electrocatalytic efficiency (5416.1 mA mg⁻¹ Pd) in a basic environment. The extraordinary electrocatalytic activity of the Pd–Ir aerogel is ascribed to the synergistic effect of Ir and unique structural characteristics of the Pd–Ir aerogel. Prevention from the degradation of stability and facile access to the active sites for reactant molecules have been guaranteed by the support-less and macroporous characteristics of the Pd–Ir aerogel, respectively. Moreover, the Ir element, as a co-metal in the structure of the Pd–Ir aerogel, acts as a very efficient promoter in the EOR and can change the electronic structure of Pd, which facilitates the electrooxidation of EtOH in alkaline media.

**EXPERIMENTAL SECTION**

**Materials.** Ethanol (C₂H₅OH), potassium hydroxide (KOH), palladium(II) chloride (PdCl₂), hydrochloric acid (HCl), and iridium(III) chloride (IrCl₃) were provided from Sigma-Aldrich Co. Palladium(II) chloride was dissolved in HCl to provide the H₂PdCl₄ precursor solution.
Physical Characterization. Both field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were applied for the identification of the structure of resultant Pd−Ir aerogel. TEM and FESEM were acquired by employing JEM-2100F (JEOL) and MIRA3 TESCAN, respectively. The data of bulk compounds and the crystallinity of Pd−Ir aerogel were recorded by employing inductively coupled plasma atomic emission spectroscopy (ICP-AES) and a D8 Advanced X-ray diffractometer (X-ray diffraction, XRD with Cu Kα irradiation source), respectively. The specific surface area of the resultant aerogel was calculated using the Brunauer–Emmett–Teller (BET, model ASAP 2020 Volumetric Adsorption, Micrometrics) equation, and the pore size distribution was determined from the desorption branches of the isotherm using the Barrett–Joyner–Halenda (BJH) theory.

Electrochemical Measurements. Same amounts (5 mg) of Pd−Ir aerogel and Pd/C were dispersed under high-power ultrasonic irradiation in 4 mL of ultrapure water and 1 mL of chitosan (1 wt %). Glassy carbon (GC) electrodes covered by the inks of Pd−Ir aerogel (2 μL) and Pd/C (5 μL) were applied as the working electrodes. To set up the glassy cell, a platinum wire and an Hg/HgO were employed as the counter and reference electrodes, respectively. To collect the electrochemistry data, a SAMAH 500 instrument was employed.

Synthesis of Pd−Ir Aerogel. A facile approach was utilized to synthesize the 3D inorganic superstructure of Pd−Ir aerogel. Briefly, the given amount of sodium borohydride (0.7 mL, 0.05M) was quickly injected into 10 mL of an aqueous solution containing 100 μL of IrCl₄ (with a concentration of 1 mg mL⁻¹) and 900 μL of H₂PdCl₄ (with a concentration 1 mg mL⁻¹) at RT (25 °C). After the reduction reaction, to induce gelation, the colloidal suspension was transferred into an oven at different temperatures (see Table 1). Next, the Pd−Ir hydrogel synthesized under optimum conditions was washed with ultrapure water, ethanol, and acetone. Finally, supercritical drying with liquid carbon dioxide was employed to dry the Pd−Ir hydrogel, and a 3D monolithic network of the Pd−Ir aerogel was achieved.

Cell Performance Test. The fuel cell (FC) efficiency tests of three catalysts were carried out utilizing a single cell with an active area of 5 cm². The membrane electrode assemblies (MEA) consisted of an anion-exchange membrane (AEM) (provided by Tokuyama Corporation) and two electrodes. A commercially available cathode catalyst, Hypermec K14 (from Acta), with a Pt loading of 2 mg cm⁻² was used as the cathode catalyst, while 1.0 mg cm⁻² of both aerogels and 5 mg cm⁻² for Pd/C (20 wt %) were loaded onto commercial carbon cloth diffusion layers as anode catalysts. A Scriber Associates Model 850e test station was used to perform the FC tests. The temperature of the FC was maintained at 25 °C, and the KOH (1.0 M)/EtOH (0.5 M) solution was pumped to the anode at a velocity of 2 mL min⁻¹.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the University of Sistan & Baluchestan for providing the facilities to perform the research.

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