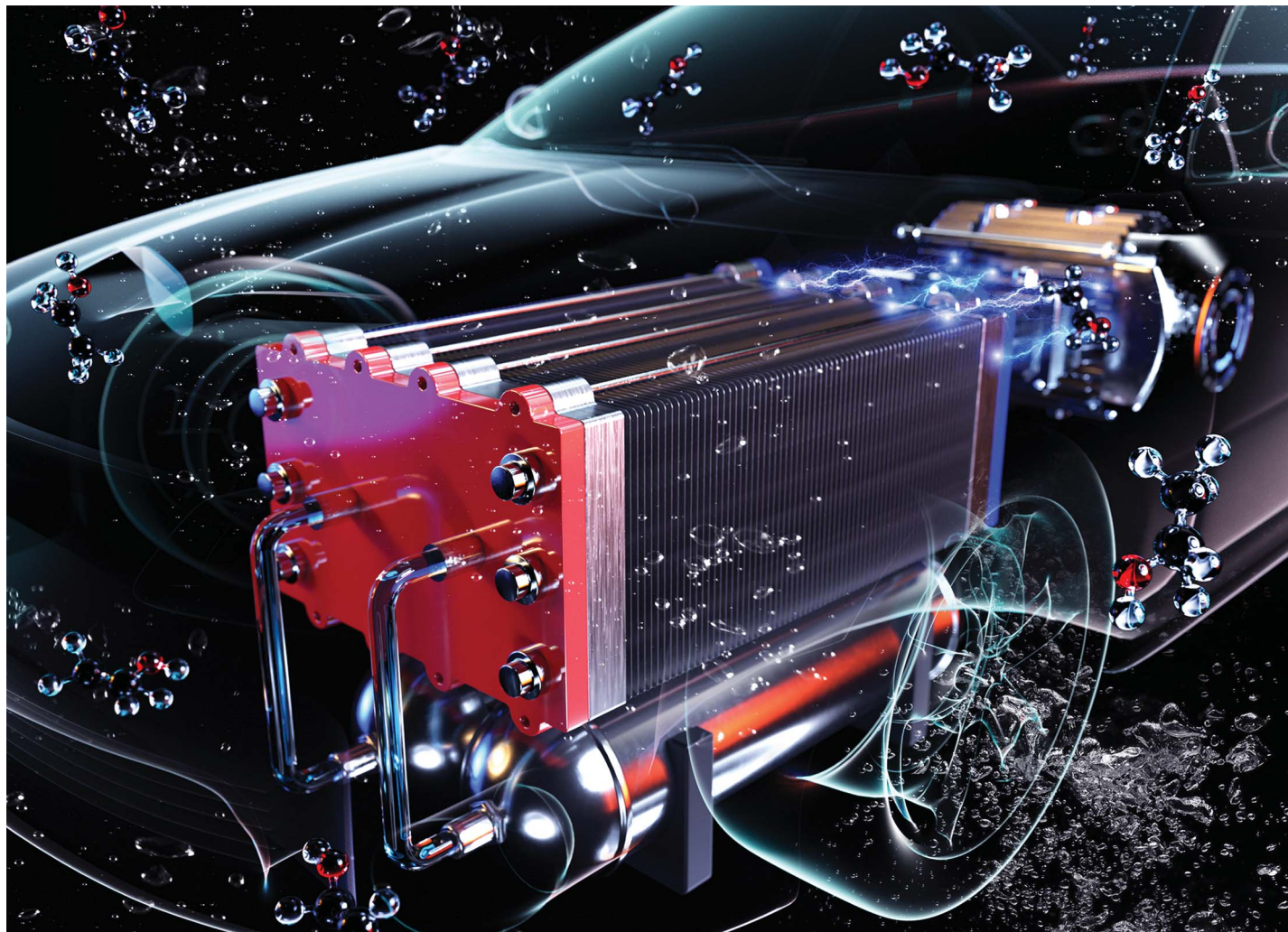




Emphasizing minimum loading of Pd for ethanol electrooxidation for state-of-the-art fuel cell application by Dr. Dimpul Konwar, Dr. Padmini Basumatary, Mr. UnHo Lee, and Prof. Young Soo Yoon at the Energy Materials Laboratory, Gachon University, South Korea.

P-doped SnFe nanocubes decorated with PdFe alloy nanoparticles for ethanol fuel cells

PdFe alloy on three-dimensional SnFeP@rGO nanocube was prepared with a low Pd content (~16% Pd). The mass activity of PdFe/SnFeP@rGO was ~17 times higher than that of commercial Pd/C (40% Pd) in ethanol fuel, which is remarkable. A single cell with PdFe/SnFeP@rGO catalyst exhibited promising power densities in both ethanol and hydrogen fuels at 60 °C and demonstrated stable operation. This catalyst can pave a new route to designing for fuel flexible cells.

As featured in:



See Young Soo Yoon *et al.*,
J. Mater. Chem. A, 2021, **9**, 10685.

PAPER

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P-doped SnFe nanocubes decorated with PdFe alloy nanoparticles for ethanol fuel cells†

Dimpul Konwar,‡ Padmini Basumatary,‡ UnHo Lee and Young Soo Yoon *

Conventional Pt-based anode catalysts in polymer electrolyte membrane fuel cells are subject to high cost, fuel inflexibility, low power and current density, and inferior stability, which hinders their application in both mobile and stationary power sources. Considering these factors, a new and novel catalyst was developed and applied to advanced fuel-flexible cells. First, P-doped SnFe nanocubes were prepared on reduced graphene oxide, then the PdFe alloy was decorated on the surface of the former and termed PdFe/SnFeP@rGO. This catalyst had a very low Pd content and achieved a remarkable mass activity enhancement of 7135.79 mA mg_{Pd}^{−1}, ~17 times higher than that of commercial Pd/C. Moreover, PdFe/SnFeP@rGO exhibited enhanced durability with no significant degradation after 1000 cycles, demonstrating its potential for application in fuel cells. A single cell with PdFe/SnFeP@rGO anode catalysts delivered maximum power densities of 60.24 and 857.54 mW cm^{−2} in ethanol and hydrogen fuel, respectively, at 60 °C.

Received 14th December 2020
Accepted 20th February 2021

DOI: 10.1039/d0ta12120g

rsc.li/materials-a

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is a green energy technology with the ability to reduce carbon footprints.^{1,2} Low-temperature operating PEMFCs with fuel flexibility (that can operate in both gaseous and liquid fuels) have a clear advantage compared with conventional PEMFCs.³ Consequently, they have gained tremendous attention for both stationary and mobile applications.^{2,4} Ethanol has one of the highest specific energy densities (8.03 kW h kg^{−1}) of the available liquid fuels; moreover, it is widely available, is liquid at ambient temperature, environmentally friendly, safe for transportation and storage, and can be produced from biomass.³ In addition, the energy density of ethanol is comparable to those of liquefied petroleum gas and gasoline.⁴ However, barriers remain against the widespread commercialization of ethanol fuel cells: a sluggish ethanol oxidation reaction leading to low performance, high cost of the components, poor long-term stability of anode catalysts, and complex oxidation reaction mechanisms.^{3,5}

Pd-based catalysts are extensively used for the oxidation of ethanol fuel, and much effort has been devoted to explore their enhanced performance for practical applications.⁶ However, their use has been obstructed by their low catalytic activity, high cost due to high Pd content, and low stability.⁷ Therefore, to

overcome these drawbacks, various new approaches have been introduced including tailoring their design through composition, alloying, and controlling the shape and size of the catalyst. Ma *et al.* reported that Pd with a cubic structure exhibited a superior electrochemical performance compared with those with rhombic dodecahedral and octahedral structures.⁸ Conversely, Yun *et al.* demonstrated that PdM (M = Cd, Zn, ZnCd) nanosheets (thickness < 5 nm) with an unconventional face-centered tetragonal phase achieved superior catalytic activities in ethanol oxidation reaction (EOR) in comparison with both monolithic Pd nanosheets and Pd/C.⁹

Alloying Pd with low-cost transition metals like PdNi,¹⁰ Pd₉₆Fe₄,¹¹ PdCu,⁵ PdSn,¹² PdCo,¹³ Pd₃Pb,¹⁴ PdZn,¹⁵ and PdMn¹⁶ can be used to modify chemical and electronic properties, which can tune the binding strength of the adsorbent on the catalyst surface.¹⁷ The incorporation of transition-metal adatoms into Pd can enhance electrocatalytic activity through four basic mechanisms. First, in the electronic effect, adatoms can change the electronic nature of active atoms.¹⁴ Second, the bifunctional effect comes into play when adatoms directly undergo catalytic oxidation or act as active co-catalysts or promoters in fuel oxidation.³ Third, the steric effect of adatoms can restrict the active atom from adsorption of strongly bound poisonous intermediates generated during the electrochemical process.¹⁸ Fourth, the ensemble effect controls the average size of Pd in the bimetallic surfaces and their uniform decoration on the support.¹⁹ Therefore, the addition of Fe to Pd can result in enhancement of the catalyst performance, as all four basic mechanisms will come into effect. To reduce the Pd content in the catalyst, Douk *et al.* developed a Pd_{89.3}–Au_{10.7} aerogel and applied less than half of its catalyst weight (2 mg cm^{−2}) in

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† Electronic supplementary information (ESI) available: XRD, BET, TEM, and electrocatalytic activity data. See DOI: 10.1039/d0ta12120g

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a single cell compared to the application of Pd/C (5 mg cm^{-2}), and obtained a current density ~ 2 times higher than that for Pd/C at 40°C in ethanol fuel.²⁰

Different Sn- and Fe-structured co-catalyst supports have attracted significant attention for use in fuel cells owing to their low cost and efficient catalytic activities.^{21,22} Furthermore, support materials with profound structures can be very effective; those with hollow structure can be particularly advantageous.²³ Recently, transition-metal-based materials such as nitrides, phosphides, sulfides, metal carbides, selenides, and phosphates have received considerable attention as new catalyst materials.^{23–25} Among them, transition-metal phosphides (TMPs) are promising catalysts because of their low cost, fast electron transport, and superior intrinsic activity.^{26,27} Binary metal phosphides such as CoMnP,²⁸ CoFeP,²⁹ NiCoP,³⁰ NiSnP,³¹ and NiFeP³² can modulate the electronic structure and bond coordination, which can lead to enhanced catalytic activities. Furthermore, the combination of bimetallic phosphides with carbon supports, such as graphene, can have enormous potential for application as multifunctional catalysts for HER, HOR, OER, ORR, MOR, and EOR.^{33,34} However, the influence of the SnFeP catalyst support on fuel cells has not been explored to date.

Again, the performance of the catalyst is not only associated with the overall composition but also depends on the size, shape, and surface distribution of the elements. These characteristics of the catalyst are crucial as they directly impact the reorganization of the active surface areas by preventing clustering or agglomeration of the catalyst nanoparticles during the test.¹⁷ Therefore, different nanostructures such as nanoflowers,³ nanosheets,⁹ nanocubes,³⁵ nanorods,³⁶ and nanowires³⁷ have been reported for the oxidation of ethanol and other hydrocarbon fuels. Yu *et al.* demonstrated unique Pd₂Sn:P/C nanorods and obtained a mass current density of $5.03 \text{ A mg}_{\text{Pd}}^{-1}$, in ethanol fuel.³⁸ Furthermore, Jayarajan *et al.* examined an amyloid fibril Pd nanocomposite catalyst for EOR, a completely new type of catalyst that can lead to advanced fuel cell design.³⁹

Electrocatalysts that can be used in both liquid and gaseous fuels have a clear advantage over conventional anodic catalysts, which can operate with only one particular fuel. Compared with those of other gaseous fuels, the oxidation of hydrogen ($\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$) in hydrogen fuel is relatively fast. Furthermore, hydrogen is a clean and sustainable form of energy and can be easily obtained by water electrolysis.⁴⁰ However, the utilization of expensive Pt materials, low catalytic activity, low durability, and material-specific comparison of figures-of-merit rather than device-specific hinder the wide-spread application of hydrogen fuel cells.⁴¹ Therefore, the development of highly active electrocatalysts through an understanding of the reaction mechanism and an increase of the mass-specific surface area by designing novel electrode structures can be very beneficial. Furthermore, non-Pt-based catalysts with superior electrochemical properties could lead to the benchmarking of state-of-the-art electrocatalysts for practical applications. Cong *et al.* designed Pd_{0.33}Ir_{0.67} nanoparticles on nitrogen-doped carbon and attained a highest power density of 514 mW cm^{-2} at 79°C .⁴² Furthermore, Miller *et al.* developed a unique C–CeO₂ support

for Pd (10 wt% Pd) nanostructured catalysts and achieved better performance for HOR compared with those of Pd/C (10 wt% Pd) and Pt/C (46 wt% Pt).⁴³ The enhanced catalytic activity was illustrated by the OH[−] donor effect of CeO₂ and strong metal-support interaction; further, a single cell with a Pd/C–CeO₂ catalyst exhibited a peak power density of 500 mW cm^{-2} .

Herein, PdFe alloy nanoparticles were successfully deposited on P-doped SnFeP@rGO (SnFeP nanocube structure, where rGO represents reduced graphene oxide) by a chemical reduction and solvothermal method. In addition, a few more catalysts were prepared following similar synthesis protocol. PdFe/SnFeP@rGO, Pd/SnFeP@rGO, PdFe/rGO, Pd/rGO, and commercial Pd/C were examined using different characterization techniques, and their electrocatalytic properties were evaluated. Their electrocatalytic properties were further compared with reported data.

2. Experimental

2.1. Synthesis of SnFeP@rGO and PdFe/SnFeP@rGO anode catalysts

All chemicals were purchased from Sigma-Aldrich (USA and Korea) and used in the synthesis without any purification. SnFeP@rGO was prepared by co-precipitation, followed by calcination. First, 0.7 g of tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and 3 M sodium hydroxide (NaOH) was dissolved in a 60 mL solution containing deionized (DI) water and ethanol (3 : 1 ratio) and stirred at 25°C for 10 min. Subsequently, 0.55 g of ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was added to the above mixture, which was then stirred for 1 h. Next, 100 mg of sodium hypophosphite monohydrate (NaH_2PO_2) was added to the mixed solution followed by stirring for 12 h at 60°C . A pale yellow precipitate was obtained, which was washed several times with DI water and ethanol, to remove the unwanted impurities, then dried at 70°C for 24 h. Next, the dried product was ground to powder and calcined at 250°C for 2 h under nitrogen atmosphere. Thus, the hollow SnFeP nanocube support was obtained and then characterized. Similarly, SnFe nanocubes were also prepared and characterized for comparison.

A further procedure was followed to prepare PdFe/SnFeP@rGO. Initially, 30 mg of the SnFeP nanocube catalyst was mixed with graphene oxide in 20 mL of a mixed aqueous solution of ethylene glycol and water, followed by mild sonication (10 min), and then stirring for 5 h. The product was filtered, dried, and termed SnFeP@rGO. Next, the PdFe/SnFeP@rGO catalyst was prepared by a solvothermal process. First, the desired amount of SnFeP@rGO nanocube support material was homogeneously dispersed in 30 mL of ethylene glycol. Subsequently, 10 mL of an aqueous solution containing sodium tetrachloropalladate (Na_2PdCl_4 , 56 mg) and iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 10 mg) was added dropwise to the SnFeP@rGO solution, followed by stirring for 2 h. Subsequently, 2 mL of hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was injected, and the solution was stirred for 4 h then subjected to solvothermal treatment at 120°C for 4 h. Next, the obtained product was washed with ethanol and DI water several times until no

impurities remained, and dried at 70 °C for 9 h, and ground to a fine powder. This fine catalyst powder was referred to as PdFe/SnFeP@rGO. Additionally, Pd/SnFeP@rGO, PdFe/SnFe@rGO, PdFe/rGO, and Pd/rGO were synthesized following a similar protocol, characterized, and evaluated for electrocatalytic activities. A commercial Pd/C catalyst (40% Pd on Vulcan XC, Premetek) was also examined.

2.2. Materials characterizations

The crystal phases of the as-synthesized catalysts were characterized using X-ray diffraction (XRD; Rigaku, Japan) using a Cu K β source. The microstructures of the catalysts were examined and recorded using scanning electron microscopy (SEM; Hitachi S-4200) and transmission electron microscopy (TEM; Tecnai G2F30) with energy-dispersive X-ray spectroscopy (EDS), selected-area electron diffraction (SAED) and elementary mapping investigations (JEOL, JEM-ARM200F). The pore size distribution and Brunauer–Emmett–Teller (BET) specific surface areas of the catalysts were determined using a surface area analyzer (Micromeritics, ASAP-2020, USA) through nitrogen isotherm measurements. The surface elemental distribution and bonding states were investigated using X-ray photoelectron spectroscopy (XPS; Thermo VG, UK) with an Al K-alpha micro-focused monochromator.

2.3. Electrochemical measurements

The electrocatalytic performances were evaluated using three-electrode cell system with a BioLogic electrochemical workstation. A modified glassy carbon electrode (GCE; 3.0 mm diameter) was used as the working electrode, platinum wire as the counter electrode and a saturated calomel electrode (SCE, Ag/AgCl, CHI 150; China) was employed as the reference electrode. Prior to starting the test, the GCE was polished with fine alumina powder (0.3 μm diameter) and washed several times with water and ethanol. The catalyst ink on the modified GCE was prepared by the following steps. First, 10 mg of the as-synthesized catalyst was dispersed in a commercial Nafion solution (5 wt%) with isopropanol (3 : 7 ratio) and sonicated for 20 min to form a homogeneous dispersion. Following this, 4 μL of the catalyst ink was dropped onto the modified GCE (catalyst loading amount: $\sim 6.9 \mu\text{g cm}^{-2}$) then the GCE was dried at 70 °C for 2 min. Electrochemical tests were performed under a N $_2$ atmosphere in a solution of 0.5 M KOH and 0.3 M ethanol (with and without ethanol) at a scan rate of 10 mV s $^{-1}$ with a potential range of -0.8 to 0.6 V. To study the durability and stability of the as-synthesized catalysts, 1000 cycles of cyclic voltammetry (CV) and chronoamperometry (CA, at 0.1 V) tests were performed. CO stripping test was done in 0.1 M KOH at a scan rate of 10 mV at room temperature (25 °C), as mentioned elsewhere.^{6,7}

2.4. Membrane electrode assembly and single cell tests

The catalyst ink was prepared by homogeneously dispersing the desired amount of catalyst powder into a solvent containing isopropanol and Nafion 117 solution (5 wt%). Subsequently, the mixture was sonicated for 20 min and then stirred for 4 h. The prepared catalyst ink was uniformly coated onto carbon paper,

which was then dried at 50 °C for 10 min. Commercial Pt/C (40 wt% of Pt, 1.6 mg cm $^{-2}$) was applied to the cathode, and a Nafion 117 (DuPont) membrane was used as the electrolyte. The Nafion 117 membrane was submerged in 2.0 M KOH for 24 h and dried at room temperature. Moreover, sandwich structures such as membrane electrode assemblies (MEAs, anode–membrane–cathode) were prepared by hot pressing at 110 °C for 2 min. A single cell had an active surface area of 5 cm ^{2} (2.5 cm ^{2} $\times$ 2.0 cm ^{2}) on both the cathode and anode sides.

For the single-cell tests in ethanol and hydrogen fuel, the fabricated MEA was inserted between two graphite serpentine flow channels. Two copper current collector electrode plates were attached to the graphitic flow channels. The cell was fixed by tightening the bolts of the stainless-steel end plates. Next, the cell measurement was performed in a fuel cell station from Scitech (South Korea). For direct-ethanol fuel cells (DEFCs), the anode side was constantly supplied with 1.0 M ethanol and 0.5 M KOH fuel at a flow rate of 5 mL min $^{-1}$ and the cathode side with humidified O $_2$ gas (200 sccm). Cell tests were performed at a constant temperature of 60 °C. Furthermore, polarization curves of the catalysts in hydrogen gas were analyzed to establish the fuel flexibility of the anode catalyst. The anode and cathode sides were fed with humidified hydrogen (100 sccm) and oxygen (200 sccm), respectively.

3. Results and discussion

3.1. Morphology and structure

The synthesis of the PdFe/SnFeP@rGO nanocube-structured catalyst is illustrated in Fig. 1, which includes the following three steps. First, SnFeP nanocubes were prepared using stoichiometric amounts of precursor materials. In the second step, a SnFeP@rGO template was prepared for the distribution and self-assembly of the nanocubes on rGO. In the final step, ultrafine PdFe nanoparticles were successfully grafted onto the SnFeP@rGO support through a solvothermal process using hydrazine monohydrate as a chemical reducing agent, thus yielding the PdFe/SnFeP@rGO catalyst.

The phase purity and crystallographic structures of the as-synthesized catalysts were investigated by powder XRD, as shown in Fig. 2 and S1.† The XRD pattern of SnFeP@rGO displays a weak and broad diffraction peak located at $\sim 25.31^\circ$, which was assigned to the (002) hexagonal phase of carbon corresponding to graphene.⁴⁴ Peaks for the alloy phases of Fe

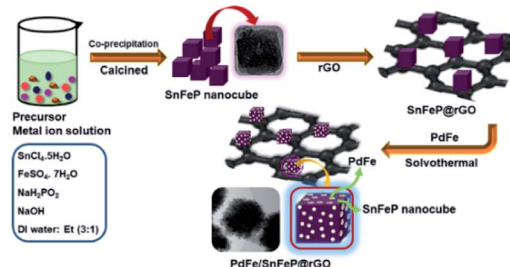


Fig. 1 Schematic representation of the PdFe/SnFeP@rGO catalyst preparation.

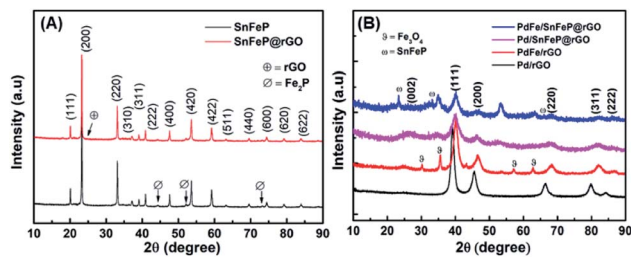


Fig. 2 Powder XRD profile of (A) SnFeP and SnFeP@rGO, and (B) as-synthesized catalysts.

and Sn are present along with those of Fe_2P and SnP_3 in SnFeP (JCPDS: 65-2595, JCPDS: 72-0853). Furthermore, the peak for the crystal phase of SnFeP resembles that of the synthetic structure of jeanduyite ($\text{FeSnO}(\text{OH})_5$, JCPDS: 31-0654). In contrast, the SnFe catalyst exhibited peaks for $\text{Fe}_{1.42}\text{Sn}_{0.43}\text{O}_3$ and cubic phase of Sn as shown in Fig. S1.† For the PdFe/SnFeP@rGO composite, different peaks appeared at 23.31° , 33.24° , 37.54° , 54.81° , and 66.12° , which were associated with the SnFeP plane, whereas the other broad and intense characteristic peaks centered at 40.42° (111), 46.78° (200), 68.58° (220), 82.97° (311), and 87.64° (222) were attributed to the crystallographic planes of Pd possessing a face-centered cubic (fcc) structure.⁴⁵ The broadening of the Pd (111) peak and minor shift to a higher degree compared to that of pure Pd (JCPDS: 46-1043) suggested that alloy formation in the Pd lattice structure and the broadening of the other peaks were due to the smaller crystal domain. In addition to the PdFe alloy phase, Pd_2Sn and PdP_3 phases were observed (JCPDS: 65-4710, and 81-7075, respectively) in PdFe/SnFeP@rGO. The Pd_2Sn and PdP_3 phases can enhance the electrochemical activity of the catalyst during EOR. Magnetite Fe_3O_4 phase that belong to $Fd\bar{3}m$ space group was also observed for PdFe/SnFeP@rGO and PdFe/rGO catalysts.²¹ Furthermore, Scherrer's equation was employed to calculate the crystallite sizes of Pd (based on the Pd (111) peak).⁴⁶ The obtained values are 3.67, 3.21, 2.84, and 2.26 nm for Pd/rGO, PdFe/rGO, Pd/SnFeP@rGO, and PdFe/SnFeP@rGO, respectively, and their lattice strain data is shown in Table ST1.†

To determine the specific surface areas of the catalysts, BET analysis was performed. The BET surface areas of all the synthesized catalysts were measured using N_2 adsorption/desorption isotherms, the results for which are shown in Fig. 3 and S2.† The BET specific surface area and pore volume

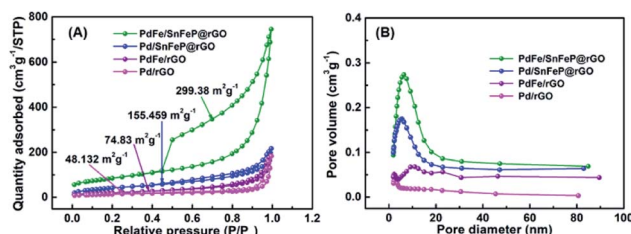


Fig. 3 (A) Nitrogen adsorption/desorption isotherms of as-synthesized catalysts, and (B) their pore size distributions.

for PdFe/SnFeP@rGO were determined to be $299.38 \text{ m}^2 \text{ g}^{-1}$ and $0.28 \text{ cm}^3 \text{ g}^{-1}$, while those for PdFe/rGO and Pd/rGO were $74.83 \text{ m}^2 \text{ g}^{-1}$ and $0.045 \text{ cm}^3 \text{ g}^{-1}$, and $48.132 \text{ m}^2 \text{ g}^{-1}$ and $0.030 \text{ cm}^3 \text{ g}^{-1}$, respectively. Furthermore, the resulting BET surface areas of SnFe, SnFeP, and SnFeP@rGO were 63.98, 94.95, and $112.24 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. S2†). The Barrett-Joyner-Halenda (BJH) adsorption isotherms were calculated as well as the pore size distribution; a large proportion of the pore diameters were noted to be between 1.6 nm to 18 nm, as shown in Fig. 3B. The high specific surface area and larger pore volume in PdFe/SnFeP@rGO was due to the incorporation of Sn, Fe, and P as promoters or co-catalysts to positively affect the electrocatalytic properties. Furthermore, a pore diameter in the range of 5–20 nm is ideal for fuel oxidation,⁴⁷ and smaller pores have the benefit of enhanced ion transport with wettability. Therefore, electrocatalytic activity can be increased by shortening the distance of the ion migration path in fuel cells.⁴⁸

The morphologies of SnFe, SnFeP, and SnFeP@rGO were examined by TEM, as shown in Fig. 4. Both SnFe and SnFeP exhibited three-dimensional nanocube structures and porous and coarse surfaces, as can be clearly observed in Fig. 4A and B. The SnFeP nanocubes ranged in size from 20 to 40 nm and were well-decorated on the rGO surface, as shown in Fig. 4C. The three-dimensional SnFeP with hierarchical pores and a coarse surface can offer the advantages of a larger electrolyte-electrode interface area, high surface area for fuel interaction, and continuous ion and electron transport paths.⁴⁹

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and EDS elemental mapping images confirmed the presence of C, O, Sn, Fe, and P in SnFeP@rGO, as shown in Fig. 4D and S3.† Moreover, the presence of P on the SnFe nanocube surface can prevent the aggregation of isolated atoms through stabilizing effects and can generate additional anchoring sites.⁵⁰

The TEM images of PdFe/SnFeP@rGO, Pd/SnFeP@rGO, PdFe/rGO, and Pd/rGO are shown in Fig. 5 and S4–S7.† These TEM images reveal that the PdFe nanoparticles were uniformly

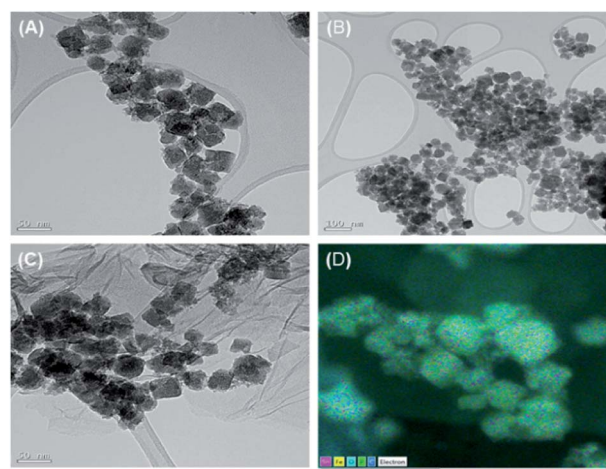


Fig. 4 TEM images of (A) SnFe, (B) SnFeP, (C) SnFeP@rGO. (D) Elemental mapping of SnFeP@rGO.

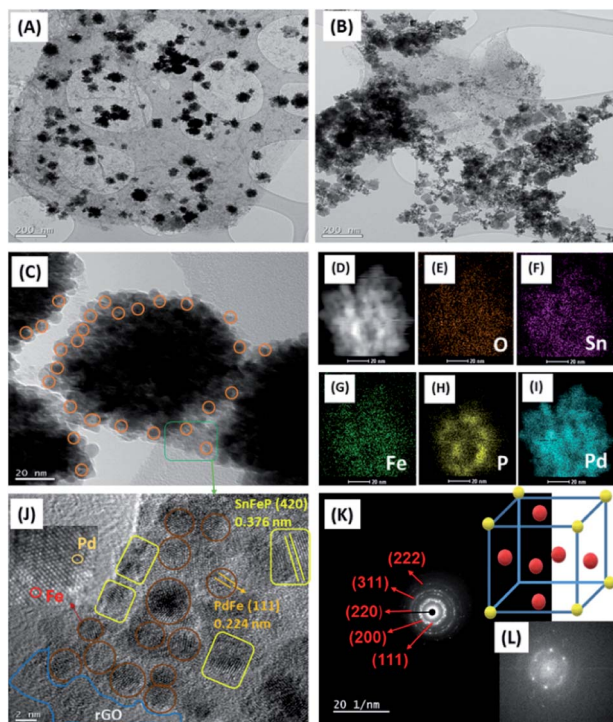


Fig. 5 TEM images of (A and C) PdFe/SnFeP@rGO and (B) Pd/SnFeP@rGO. (D–I) HAADF-STEM image and elemental mapping of PdFe/SnFeP@rGO. (J) HR-TEM of PdFe/SnFeP@rGO. (K) SAED pattern and (L) fast Fourier transform (FFT) of PdFe/SnFeP@rGO. The face-centered cubic (fcc) structure model of PdFe is obtained from FFT.

dispersed over the entire surface of the SnFeP@rGO nanocubic structure, as shown in Fig. 5A. Conversely, Pd nanoparticles in Pd/SnFeP@rGO displayed a high degree of agglomeration and did not properly attach to the SnFeP nanocube support (Fig. 5B). The high-resolution (HR-TEM) images (Fig. 5C, J and S6†) of PdFe/SnFeP@rGO revealed that the PdFe alloy nanoparticles had an average particle size of 2.2 nm (calculated using ImageJ software) and were homogeneously and well dispersed throughout the surface of the SnFeP@rGO nanocube template. Their *d*-spacings were measured to be 0.224 (111) and 0.376 nm (420), which correlate to crystal planes of PdFe and SnFeP, respectively. HAADF-STEM (Fig. 5D, S5 and S6†) and elemental mapping (Fig. 5E–I) of PdFe/SnFeP@rGO further confirmed that PdFe alloy nanoparticles were well-distributed on the surface of SnFeP@rGO nanocubes. Contrarily, the nanoparticles of PdFe/SnFe@rGO, PdFe/rGO, and Pd/rGO displayed a higher degree of cluster formation and agglomeration (Fig. S4 and S7†). The average particle size of PdFe in PdFe/rGO was 3.21 nm, while that of Pd in Pd/rGO was 2.85 nm. The SAED pattern shown in Fig. 5K confirms the crystallographic planes of PdFe and matches well with that of the powder XRD data. From the fast Fourier transform (FFT), it is evident that the PdFe alloy had a fcc structure. A typical fcc schematic model is further depicted as a reference.

XPS measurements were carried out to investigate the electronic interactions, elemental compositions, and chemical oxidation states of the different elements of the synthesized

catalysts, as shown in Fig. 6. The survey scan of PdFe/SnFeP@rGO confirms the existence of C (graphene), O, Sn, Fe, P, and Pd, as shown in Fig. 6A. The fitted peaks of Pd 3d at 334.90 and 340.19 eV were assigned to the 3d_{5/2} and 3d_{3/2} orbitals of the metallic Pd⁰ state; this indicates that metallic Pd⁰ suppressed Pd²⁺, revealing that Pd⁰ is the primary chemical (metallic) state on the surface of the PdFe/SnFeP@rGO catalyst. The other distinguishable peaks, located at 336.5 and 341.71 eV were attributed to Pd²⁺ mainly in the Pd(OH)₂ and PdO species, respectively, on the catalyst surface, as shown in Fig. 6B. The distinct peaks located at 484.93 (3d_{5/2}) and 493.41 eV (3d_{3/2}) were assigned to metallic Sn⁰. Additional peaks observed at 486.32 (3d_{5/2}) and 494.67 eV (3d_{3/2}) correspond to oxidized Sn (Sn²⁺, SnO), as shown in Fig. 6C.^{53,54}

Furthermore, the Fe 2p spectra (Fig. 6D) peaks at 710.26 (2p_{3/2}), 723.74 (2p_{1/2}), 712.80 (2p_{3/2}), and 726.03 eV (2p_{1/2}) were assigned to the oxidized Fe (Fe²⁺ and Fe³⁺) species that formed on the catalyst surface.^{55,56} The characteristic peaks centered at 129.22 and 132.81 eV correspond to the metallic P⁰ and oxidized P⁺ (P₂O₅) species,⁵⁷ respectively, as shown in Fig. 6E. Another reflecting peak at 137.16 eV was attributed to P–O caused by the partial oxidation of the PdFe/SnFeP@rGO surface, which arose owing to air exposure.^{58–60} A comparison of binding energy shifting for Pd 3d_{5/2} and 3d_{3/2} for the catalysts are shown in Table S2.† The Pd 3d_{5/2} peaks of PdFe/SnFeP@rGO exhibited a minor shift toward higher binding energies (BEs) compared to those of Pd/C. This positive BE shift (Fig. 6F) of Pd (0.55 eV, Table S2†) reveals that there are electronic interactions involving the transition metal P, Sn, rGO, Fe, and Pd atoms within the PdFe/SnFeP@rGO catalyst. This interaction modifies the electronic states of the Pd structure, thus providing PdFe/SnFeP@rGO with excellent catalytic activity, strong resistance to CO poisoning, and a large electrochemical surface area.

3.2. Electrochemical performance

The electrocatalytic activities of the as-synthesized anode catalysts were examined in a 0.5 M KOH solution, as shown in Fig. 7A, in a potential range of –0.8 to +0.6 V (vs. Ag/AgCl electrode) at a scan rate of 10 mV s^{–1}. The electrochemical

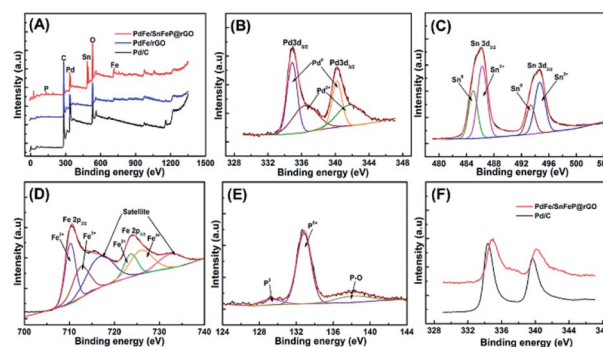


Fig. 6 (A) Survey scan of PdFe/SnFeP@rGO, PdFe/rGO, and Pd/C catalysts. XPS spectra of (B) Pd 3d, (C) Sn 3d, (D) Fe 2p, and (E) P 2p of PdFe/SnFeP@rGO. (F) Comparison of Pd 3d spectra of PdFe/SnFeP@rGO and Pd/C.

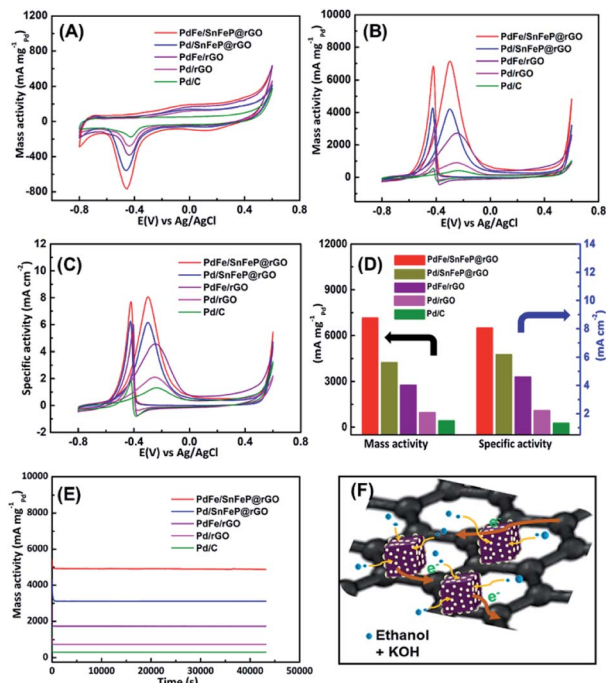


Fig. 7 (A) CV curves of PdFe/SnFeP@rGO, Pd/SnFeP@rGO, PdFe/rGO, Pd/rGO, and Pd/C catalysts in 0.5 M KOH solution at a scan rate of 10 mV s^{-1} . (B) Mass activity peaks of as-synthesized catalysts recorded in 0.5 M KOH and 0.3 M ethanol aqueous solution with a scan rate of 10 mV s^{-1} . (C) Specific activity, and (D) comparison of specific and mass activities. (E) Chronoamperometric data recorded at $0.1 \text{ V vs. Ag/AgCl}$ in 0.5 M KOH and 0.3 M ethanol solution for 12 h. (F) Schematic representation of the PdFe/SnFeP@rGO electrochemical activity toward EOR.

surface areas (ECSAs, in units of $\text{m}^2 \text{g}^{-1}$) of the catalysts were calculated using the following equation: $\text{ECSA} = q_s / (0.405 \times Q_{\text{Pd}})$,^{59,61} where q_s is determined by integrating the reduction peak area (in the CV curves) of the PdO monolayer and Q_{Pd} is the Pd loading (in units of $\mu\text{g cm}^{-2}$) on the working electrode. Meanwhile, 0.405 mC cm^{-2} was the charge necessary for the reduction of the PdO monolayer. The ECSA of PdFe/SnFeP@rGO ($88.65 \text{ m}^2 \text{g}^{-1}$) was higher than those of the Pd/SnFeP@rGO (68.32), PdFe/SnFe@rGO (60.05), PdFe/rGO (59.74), Pd/rGO (42.89), and Pd/C ($31.47 \text{ m}^2 \text{g}^{-1}$) catalysts. This result implies that the PdFe/SnFeP@rGO catalyst has abundant exposed electrocatalytic sites compared with the other catalysts.

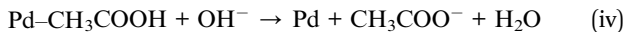
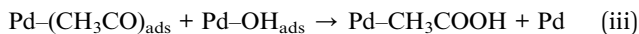
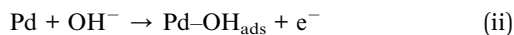
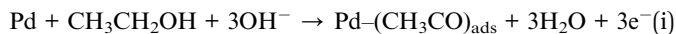
The EOR activities of the synthesized catalysts were examined in an alkaline solution comprising 0.5 M KOH and 0.3 M ethanol, as shown in Fig. 7B and S8A.† All the synthesized anodic catalysts displayed twin distinct oxidation anodic peaks, which relate to the forward current (I_f) peaks and the reverse current (I_r) peaks, respectively. Generally, the I_f peaks is assigned to the oxidation of ethanol molecules and the I_r peaks to the adsorption of intermediate species such as CH_x , CO_{ad} , acetaldehyde, acetic acid, and acetate. The relatively sharp I_r peak for PdFe/SnFeP@rGO indicates fast reduction of PdO layer ($\text{Pd-O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Pd} + 2\text{OH}^-$).⁶² Besides, I_r peak corresponds to freshly chemisorbed species of OH_{ads} of ethanol and

not because of the carbonaceous species.⁶² However, if the I_r peak is high along with a positive shift of peak potential at higher scan rates, then there is a greater possibility of catalyst poisoning as it can be directly related to the carbonaceous species.⁶³ Again, there is a hypothesis that a catalyst with $I_f/I_r > 1$ is less susceptible to poisoning from the intermediate species generated during EOR, which is not quite relevant.^{63,64} PdFe/SnFeP@rGO further exhibited an onset potential (E_{onset}) and mass activity of -0.57 V and $7135.79 \text{ mA mg}_{\text{Pd}}^{-1}$, respectively. The mass activity of PdFe/SnFeP@rGO were 1.68, 2.59, 7.54, and 17.27 times higher than those of Pd/SnFeP@rGO (4228.40), PdFe/rGO (2746.56), Pd/rGO (945.21), and Pd/C ($413.16 \text{ mA mg}_{\text{Pd}}^{-1}$), respectively. The E_{onset} of the PdFe/SnFeP@rGO catalyst was shifted to a more negative potential than those of the other catalysts as shown in Table ST3,† indicating a better oxidizing ability and superior catalytic activity towards EOR. Additionally, the onset potential of PdFe/SnFeP@rGO was -0.51 V (Table ST3†), with a mass activity of $3431.08 \text{ mA mg}_{\text{Pd}}^{-1}$, which is 2.07 times lower than that of PdFe/SnFeP@rGO. This indicates that more charge carriers can be generated *via* P-atom doping, thereby improving the electrical conductivity of SnFe. Similar results were reported by Bao *et al.* for Pd@FeP in formic acid electrochemical oxidation.⁶⁵ Furthermore, PdFe/SnFeP@rGO displayed a very high mass activity compared with other reported data for Pd-based catalysts applied to EOR (Table ST4†). Therefore, this study is primarily focused on the PdFe/SnFeP@rGO catalyst.

The specific activity of the catalysts displays a similar trend to that of the mass activity, as shown in Fig. 7C. The following order was observed: PdFe/SnFeP@rGO (8.04 mA cm^{-2}) > Pd/SnFeP@rGO (6.18) > PdFe/rGO (4.59) > Pd/rGO (2.20) > Pd/C (1.31 mA cm^{-2}). The superior specific activity of PdFe/SnFeP@rGO could be due to the following reasons. The surface electronic modification of Pd upon doping of Fe in PdFe/SnFeP@rGO was confirmed from the XPS investigation, which revealed the dominance of metallic Pd, along with Fe^{2+} and Fe^{3+} . Again, a relatively higher lattice strain of the catalyst was further validated from XRD (Table ST1†). Thus, the bifunctional and strain effects in the bimetallic Pd-Fe alloy played a critical role in the enhancement of the specific activity of the PdFe/SnFeP@rGO compared with other catalysts towards EOR.^{66,67} Furthermore, Pd-Fe anchored on P-doped SnFe support not only leads to the fast electron transfer but also increases the stability in alkaline medium by limiting the adsorption of undesired reactant product.^{65,68} The bimetallic phosphide SnFeP, along with phases of PdP_3 and Pd_2Sn (confirmed from XRD) can also increase the catalytic activity by reducing the free energy required for protonation and by controlling the transfer of electrons evolved in the reaction process towards a particular direction, thereby generating a synergistic effect of the catalyst during EOR.^{32,69,70}

Therefore, the introduction of SnFeP as a support material is an effective strategy to improve the Pd-based activity for EOR. For a better understanding of charge transfer between nanocube and graphene a schematic of the EOR by PdFe/SnFeP@rGO, in which the electrons generated were transferred *via* graphene support, is shown in Fig. 7F. Besides, the

electrooxidation of ethanol by a Pd-based catalyst can undergo the following mechanism:



The Tafel slope was calculated from linear scanning voltammetry (in 0.5 M KOH) measurements at a low scan rate of 2 mV s⁻¹, as shown in Fig. S9.† The Tafel slopes of PdFe/SnFeP@rGO, PdFe/rGO, Pd/rGO, and Pd/C were 78, 151, 172, and 212 mV dec⁻¹, respectively. In addition, the overpotential of PdFe/SnFeP@rGO was merely 180 mV compared with 289, 306, and 346 mV for PdFe/rGO, Pd/rGO, and Pd/C, respectively. This confirms the faster reaction kinetics of PdFe/SnFeP@rGO than that of other catalysts.

The long-term stabilities of the catalysts toward EOR were investigated by chronoamperometric measurements in 0.5 M KOH with and without 0.3 M ethanol at a constant potential of 0.1 V (vs. Ag/AgCl) for 12 h, as shown in Fig. 7E and S8B.† The PdFe/SnFeP@rGO catalysts achieved the highest oxidation current densities and demonstrated superior stability compared to the other catalysts. The initial oxidation current was higher because of double-layer charging and ample active sites for ethanol activation or atomic rearrangement of metals. However, the minute decrease in the oxidation current density over time was related to catalyst surface changes and formation of unwanted intermediate species that blocked the active surface sites of the catalyst.^{59,71} PdFe/SnFeP@rGO exhibited lower activity decay than the other as-synthesized catalysts, confirming its strongest resistance against CO poisoning and excellent durability toward EOR. Furthermore, long-term potential cycling tests were completed by performing CV for 1000 cycles, as shown in Fig. S10.† At the end of the cycling, PdFe/SnFeP@rGO achieved a high chemical stability and maintained an oxidation current of 84.8%, which is higher than those of PdFe/rGO (58.1%) and Pd/C (34.59%), respectively. These results reveal that the PdFe/SnFeP@rGO catalyst is extremely stable for EOR in an alkaline medium.

The influence of the scan rate was analyzed to study the electrochemical reaction mechanism of the PdFe/SnFeP@rGO, PdFe/rGO, and Pd/C catalysts toward EOR, the results for which are shown in Fig. S11.† The catalysts were evaluated at various scan rates ranging from 10 to 150 mV s⁻¹ in a 0.5 M KOH and 0.3 M ethanol solution. The forward oxidation current peak increased with a continuous increase in the potential scan rate. Additionally, the forward peak current (*I_f*) in the cyclic voltammogram displayed a potential shift, revealing the occurrence of an ohmic drop at high current. The plot of *I_f* linearly increased (Fig. S11B, D and F†) with the square root of the potential scan rate, indicating the electrocatalysis stability and demonstrating that the EOR of the synthesized electrode surface was an electrochemical diffusion-controlled process,

according to the Randles-Sevcik model.⁷² These results also imply that electron transfer took place directly between the PdFe/SnFeP@rGO catalyst and electrons generated from EOR. Furthermore, this catalyst exhibited the largest slope of 371.85, compared to those of PdFe/rGO (84.17) and Pd/C (54.77), respectively, suggesting that it has the highest electron transfer coefficient rate, which is a rate-determining step.

CO is considered as a primary poison species for the catalysts that undergo methanol or ethanol electrooxidation.^{71,73} Therefore, the CO stripping test could interpret as a prototype to evaluate the CO tolerance and desorption ability (from carbonaceous intermediates) of a respective catalyst. The CO stripping of PdFe/SnFeP@rGO and Pd/C in 0.1 M KOH is shown in Fig. S12.† For Pd/C a broad peak current was observed from 0.19 to 0.46 V. On the other hand, for the first positive scan, a relatively sharp peak with high current density was noticed for PdFe/SnFeP@rGO, which was related to the oxidation of pre-adsorbed CO.⁷ This peak disappeared in the next subsequent scan due to the removal of the adsorbed CO and other intermediates. The onset potential for PdFe/SnFeP@rGO was 0.13 V, while Pd/C was 0.21 V. The lowest onset potential reported was 0.225 V for PtPd/RGO (PtPd nanocube) catalyst.⁷³ This signifies that PdFe/SnFeP@rGO is active for CO oxidation and also has better CO tolerance than Pd/C.^{6,71} To examine the stability of the nanocube structure and PdFe alloy characteristics, TEM analysis was performed after CO stripping test and is shown in Fig. S13.† PdFe/SnFeP@rGO did not show any major structural alteration after the CO test. However, a minor change in *d*-spacing (marked in green color) was identified after the test that may be related to atomic rearrangement within the catalyst (PdFe alloy).⁷⁴

3.3. Single cell performance

The DEFC polarization curve with single-cell anode catalysts was investigated under constant operating temperature of 60 °C, as shown in Fig. 8A, B and S14.† It was clearly observed

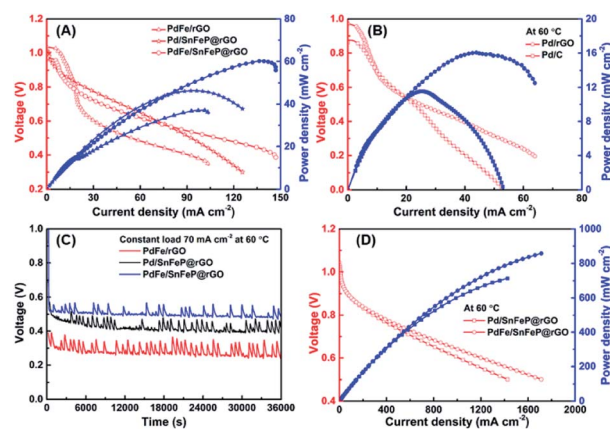


Fig. 8 (A and B) Polarization curves of DEFCs using different anode catalysts at 60 °C with 0.5 M KOH and 1.0 M ethanol. (C) Stability test for DEFCs at a load current density of 70 mA cm⁻² at 60 °C in 0.5 M KOH and 1.0 M ethanol solution as fuel. (D) Polarization curves of PdFe/SnFeP@rGO and Pd/SnFeP@rGO in hydrogen fuel at 60 °C.

(Fig. S14†) that the open-circuit voltage and maximum power density (MPD) of PdFe/SnFeP@rGO significantly increased with the addition of KOH. The increase from 14.85 to 60.24 mW cm⁻² occurred because of the concomitant increase in the electrochemical redox reaction rates and superior voltage retention.⁷⁵ The MPD of PdFe/SnFeP@rGO was almost 1.67, 3.75, and 5.22 times higher than those of PdFe/rGO (37.08), Pd/rGO (16.05), and Pd/C (11.54 mW cm⁻²), as interpreted from Fig. 8A and B. Furthermore, a comparison of Pd-based catalysts in DEFCs with recently reported data is shown in Table S5,† which indicates that PdFe/SnFeP@rGO has superior electrocatalytic activity toward DEFCs. The outstanding performance of this catalyst can be attributed to several aspects. First, PdFe was dispersed uniformly on the SnFeP@rGO surface without any agglomeration. Second, doping with P atoms could modulate the electronic state of SnFe to enhance its chemical and intrinsic electric conductivity, which will contribute to a faster electron transfer, thereby leading to the improvement of the electrochemical performance toward EOR.⁷⁶ Third, the presence of intermediate states such as Pd₂Sn, PdP₃, FeP, and SnP₃ (as confirmed phases from XRD) can initiate an efficient bifunctional mechanism for enhancing the electrochemical properties during EOR.^{77–80} Finally, owing to the ensemble effect, the average size of Pd in the bimetallic alloy can be controlled (~2.2 nm) and Pd alloy can be uniformly decorated on the three-dimensional nanocube support.

Furthermore, stability measurements of the single cells were conducted at a constant load current density of 70 mA cm⁻² at 60 °C. Initially, the PdFe/SnFeP@rGO cell voltage declined to 0.53 V until 1000 s; subsequently, it remained stable for 10 h, as shown in Fig. 8C, demonstrating its higher efficiency due to the fast removal of the adsorbing intermediate species from Pd active sites. In contrast, the Pd/SnFeP@rGO and PdFe/rGO cells also remained stable but with lower voltages. In addition, the stability of PdFe/SnFeP@rGO (at load current density, 100 mA cm⁻²) and fresh Pd/C (40 mA cm⁻²) single cells were examined, as shown in Fig. S15.† The single cell with a Pd/C catalyst completely deteriorated after 12 h, whereas the PdFe/SnFeP@rGO cell remained stable and exhibited a very minimal voltage decline from 0.42 to 0.39 V at 60 °C.

To examine the fuel flexibility of the single cells, they were further run in hydrogen gas; their polarization curves are shown in Fig. 8D and S16.† A single cell with PdFe/SnFeP@rGO exhibited an MPD of 857.54 mW cm⁻² at 60 °C, while single cells with Pd/SnFeP@rGO, PdFe/rGO, and Pd/C delivered MPD values of 714.08, 456.15, and 200.64 mA cm⁻², respectively. A comparison of recent Pd-based anode catalysts in hydrogen fuel is shown in Table S6.† From the table, it is evident that the electrochemical performance of the PdFe/SnFeP@rGO catalyst is far superior to that of earlier reports and that this catalyst can be applied in fuel-flexible cells and as cathode catalysts for thermal batteries.^{81,82} Furthermore, because of the superior electronic interactions of PdFe and SnFeP@rGO, they can also be used as electrode for supercapacitors and other state-of-the-art flexible wearable devices.^{83–87}

4. Conclusions

In conclusion, this study demonstrates a simple and economical method to synthesize a PdFe/SnFeP@rGO catalyst. This catalyst has a potential fuel flexibility (employed to liquid and gaseous fuels) and can be applied to both stationary and portable fuel cell stations. The SnFeP@rGO nanocubes were demonstrated to be effective supporting templates for a new catalyst design and application. The PdFe/SnFeP@rGO catalyst achieved superior catalytic activities and stabilities compared to those of the Pd/SnFeP@rGO, PdFe/rGO, Pd/rGO, and Pd/C catalysts. The surface configurations of the PdFe alloy are highly responsible for the improved electrocatalytic activity in the EOR, which can be attributed to the lowest overpotential (0.180 V) among the synthesized catalysts. Therefore, the superior durability and high activity of PdFe/SnFeP@rGO with fuel flexibility makes it a promising catalyst for low-temperature fuel cells.

Author contributions

D. Konwar conceptualized the catalyst design, carried out experimental work, and wrote the manuscript. P. Basumatary performed catalysts preparation, data curation, and wrote the draft version of the article. U. H. Lee prepared the project report and assisted in the revision. Y. S. Yoon supervised the project and guided throughout the study.

Conflicts of interest

The authors states that there are no conflicts to declare.

Acknowledgements

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the grant was funded by the Korean Government of Ministry of Knowledge Economy (No. 20194030202440). This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MSIT) (No. NRF-2019M2D1A1079208).

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