



Conductivity-tailored PtNi/MoS₂ 3D nanoflower catalyst via Sc doping as a hybrid anode for a variety of hydrocarbon fuels in proton exchange membrane fuel cells

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ARTICLE INFO

Keywords:

Hybrid catalyst
Ethanol
Methane
Hydrogen
Biogas

ABSTRACT

A novel and unique PtSc_{0.5}Ni/MoS₂@graphene catalyst possessing hybrid characteristics is prepared. Initially, three-dimensional nanoflower-like structures of MoS₂ are deposited onto graphene sheets, and then PtScNi nanoparticles are grafted onto the MoS₂@graphene support. For optimization, catalysts with different doping ratios ($x = 0.2, 0.5$, and 1.0) of Sc are prepared and examined. The electrochemical performances of PtNi/MoS₂@graphene, Pt@graphene, and commercial Pt/C catalysts are further evaluated for comparison. A single cell with the PtSc_{0.5}Ni/MoS₂@graphene catalyst exhibits a maximum power density of 51.70 mW cm^{-2} at 50°C in ethanol fuel, which is higher than previously reported values. The cell with commercial Pt/C catalyst, in contrast, displays a power density ~ 3.7 times lower. Furthermore, the PtSc_{0.5}Ni/MoS₂@graphene catalyzed single cell delivers promising power densities and stabilities in methane and synthetic biogas fuel containing CH₄, CO₂, and H₂S.

1. Introduction

Fuel cells generate electrical energy by electrochemical transformation of a specific fuel's potential energy. Therefore, fuel cells possessing fuel flexibility at low temperature can be very promising. In this context, research has been conducted on different catalysts and their supporting materials to achieve higher catalytic efficiency. With nanoparticle catalysts, low catalysts utilization is a major hindrance towards attaining a high performance for proton-exchange membrane (PEM) fuel cells [1]. A conventional anode catalyst in the fuel cells only conducts electrons, and the triple-phase boundary is limited to the thin anode-membrane interface. However, a hybrid anode catalyst combines the properties of mixed ions and electron conductivity and has both a larger electrochemical active surface area because of the ordered structure and an enhanced triple-phase boundary that can lead to superior catalytic activities [1,2]. In other words, high efficiency and reliability can be achieved by using hybrid catalysts because of their synergistic and bifunctional effects [3]. Further, the hybrid catalysts can decrease anodic overpotential while having the fuel flexibility to use either liquid or gaseous fuels. Therefore, developing a hybrid anode catalyst for PEM fuel cells will be highly beneficial.

Ethanol, which could be applied in fuel cells at low temperatures ($50\text{--}90^\circ\text{C}$), [4] surpasses other candidates by having a relatively high energy density (8030 W h kg^{-1}) and low toxicity, in addition to being non-corrosive, very low pollution risk, ease to handle and store, low cost, and the ability to be produced from biomass [4,5]. However, the wide-spread commercialization of direct ethanol fuel cells (DEFCs) is being hindered by the low performance, high costs, and poor stability of anode catalysts [6,7]. Combinations of different materials have been considered for the anode catalysts, noble metals on carbon supports and oxide-supported transition metals, and noble metals doped with low-cost transition metals [7,8]. Pt catalysts are widely used in ethanol-based fuel cells. However, high cost, very limited presence, and their significantly suffering from poor cycle life due to their susceptibility to poisoning by CO and CHO produced during ethanol oxidation are the major obstacles [6].

Different noble and transition metals (such as Ru, Rh, Pd, and Mo) have been used to modify the electronic and structural properties of Pt in order to improve the catalytic efficiency and durability [9–12]. Bi-metallic Pt-based catalysts can deliver enhanced catalytic activity, but at the cost of limited capability [13]. Recently, nanomaterials with ternary compositions (Pt–Sn–Ni, Pt–Sn–Co, Pt–Sn–Rh, Pt–Rh–Ni,

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<https://doi.org/10.1016/j.apcatb.2020.118724>

Received 16 October 2019; Received in revised form 30 January 2020; Accepted 2 February 2020

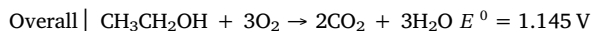
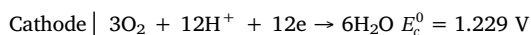
Available online 03 February 2020

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Pt–Mo–Ni, and Pt–Co–Fe), and structural profundity have shown promising electrocatalytic activity compared to their binary counterparts [13–18]. However, the combination of Pt–Sc–Ni has not yet been studied in this respect, even though scandium oxide is known to possess high ionic conductivity and can increase the electrocatalytic activity [19]. The doping of Sc into the catalyst could generate oxygen vacancies that may improve ionic conductivity at the electrode-electrolyte interface [19,20]. Also, polycrystalline Pt₃Sc catalysts are known to enhance the electrochemical performance by 1.5–1.8 times compared to pure Pt [21]. Still, the amount of Sc within the catalyst remains to be optimized, or the electronic conductivity at the electrodes could suffer [19]. The addition of Ni into the catalyst could also be beneficial because it converts readily to Ni(OH)₂. The redox centers of Ni²⁺ and Ni³⁺ can exhibit significant catalytic activity towards the ethanol oxidation reaction (EOR) [22]. Furthermore, the inclusion of Mo could reduce the adsorption of CO/CHO on the electrocatalytic sites of Pt [23].

The development of highly efficient electrocatalysts requires the design of catalyst supports that need to be considered. Graphene is a very promising support among the all carbon-based materials [24]. The graphene support permits high catalyst loading because of its larger surface area, together with relatively high electron conductivity and high mechanical and chemical stability. Furthermore, the two-dimensional structure and superior thermal conductivity of graphene, combined with its ability to make interfacial modification easily can enhance the overall performance of the catalyst [24,25]. However, during electrode assembly, the graphene sheets may be stacked together and become agglomerated, thereby limiting the surface area and depleting the electro-active sites [26]. Adding a three dimensional MoS₂ co-support onto the graphene sheets could overcome this problem by widening the distance between the sheets [27]. Furthermore, the synergistic effect of MoS₂ can also enhance the electrocatalytic activity [28].

As mentioned above, the anode catalyst primarily determines the performance of a single cell. Therefore, anode catalysts with high durability, stability, and superior catalytic activity towards EOR are highly desirable. Theoretically, an ethanol molecule can release twelve electrons, however in practical EOR only four electrons are released because complete oxidation has to overcome the splitting of C–C bond, which is energetically unfeasible at low temperature [29]. Specifically, the following electrochemical reactions can occur when using ethanol fuel in a PEM fuel cell:

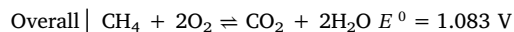
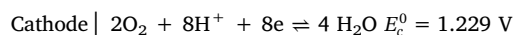
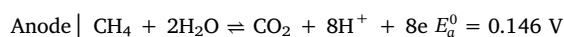


In advanced catalyst design, structural modifications are also commonly used to further improve the electrocatalytic activities. Therefore, anode catalysts with a variety of structures, such as nanowire, nanoflower, nanotube, and nanosphere have been reported [30]. Of these structures, the smaller spherical nanoparticles or nanospheres have the largest surface area and exhibit superior electrocatalytic activities [31]. Besides, the structural support can enhance the catalyst performance by preventing coalescence, agglomeration, and Ostwald ripening of the nanoparticles [32]. For ethanol, one study reported a power density of 25.1 mW cm⁻² at 90 °C using a novel PtSn/C anode catalyst, [33] whereas in a separate study researchers grew Pt nanocrystals on three-dimensional (3D) graphene and MoS₂ nanosheets for use in hydrogen evolution and alcohol oxidation reactions [34].

Advanced multifunctional or hybrid anode catalysts can operate with hydrogen fuel containing impurities and deliver superior electrochemical performance. US department of energy (US, DOE) recommends that PEM fuel cells need to achieve the technical targets

(0.3 g/kW Pt loading, and 55% energy conversion efficiency) by 2025 for hydrogen fuel containing trace impurities of H₂S = 10 ppb, CO = 0.1 ppm, CO₂ = 5 ppm, and NH₃ = 1 ppm). For Pt/C (20 wt% Pt) catalyst Prass et al. tested 0.2 ppm CO and 4 ppb of H₂S impurity for hydrogen fuel [35]. For a single cell, they reported a voltage drop of ~40–50% in 10 h at a constant load of 1.0 A cm⁻² in 0.2 ppm CO impurity but, for 4 ppb of H₂S, negligible voltage drop was recorded.

Further, the current dependence on non-renewable energy can be significantly decreased if the abundant natural gas and biogas can be used in low-temperature PEM fuel cells. The primary components of biogas are (55–75%) CH₄ and (30–45 %)CO₂, with the minor constituents of (0–1 %) H₂S, NH₃, (0–1 %) N₂, and (0–2 %) H₂ [36]. The H₂S impurity can significantly degrade cell performance due to sulfur poisoning, making it challenging to operate the cell for long term [37]. Further H₂S has direct influence on Pt loading as reported by Hashimasa et al. [38]. In biogas the primary anodic reaction is methane oxidation. At 25 °C, the following electrochemical reactions occur when using humidified methane in a fuel cell:



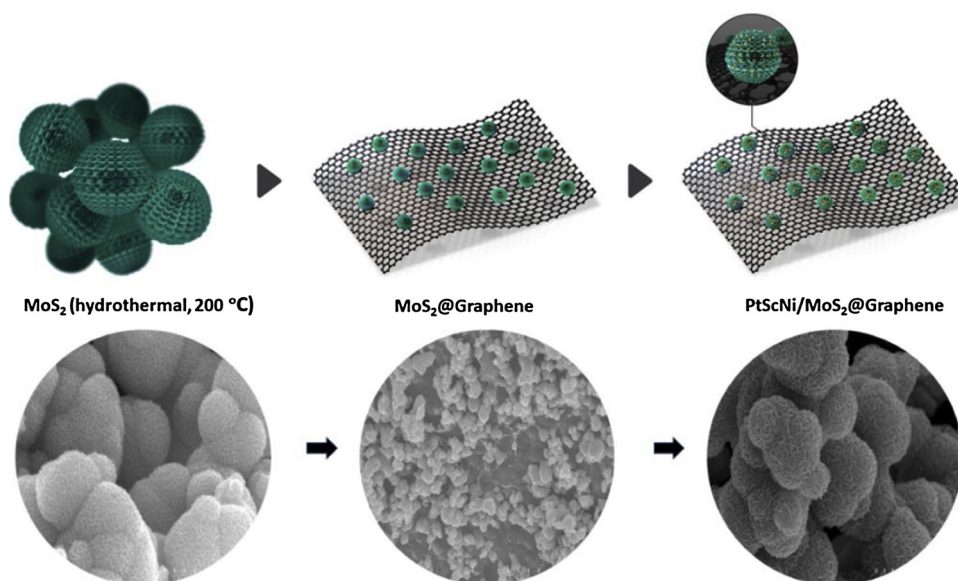
A direct methane fuel cell operating at low temperature with Pt-organometallic complexes on ordered mesoporous carbon has achieved a power density of ~29.4 μW cm⁻² at 80 °C [39]. Recently, alkaline fuel cells with special Gortex-based electrodes were reported to reach 21.6 mW cm⁻² using mixed methane and hydrogen fuel [40]. Herein, novel ternary PtSc_{0.5}Ni nanoparticles on 3D nanoflower MoS₂@graphene support were synthesized as a hybrid anode catalyst for the electrooxidation of ethanol, hydrogen, methane, and biogas. The hybrid PtSc_{0.5}Ni/MoS₂@graphene catalyst displayed mixed ion and electron conduction in the anode, and exhibited promising catalytic performance towards ethanol, hydrogen, methane, and biogas containing H₂S (2%). These results suggest a new direction in electrocatalysts development.

2. Experimental section

2.1. Catalyst fabrication

MoS₂@graphene was prepared using a two-step synthesis process. At first, flower-like MoS₂ template was prepared. Briefly, 25 ml of 0.02 M aqueous thiourea was mixed with 25 ml of 0.02 M aqueous ammonium molybdate by constant stirring. The resulting mixed solution was then transferred to a Teflon-lined vessel, sealed, and heated at a temperature at 200 °C for 15 h. After this hydrothermal treatment, the product was centrifuged, washed several times with deionized (DI) water and ethanol, and dried overnight at 70 °C. Next, the desired amount of as-prepared MoS₂ catalyst was mixed with graphene and gently sonicated for 20 min in 15 ml of a water and ethanol mixture. This mixed solution was then stirred for 2 h, and left overnight at 70 °C under vacuum atmosphere to allow the solvents to evaporate.

The PtSc_{0.5}Ni/MoS₂@graphene anode catalyst was synthesized via a solvothermal method. Briefly, the desired amount of as-prepared MoS₂@graphene was dispersed in ethylene glycol. Next, a 50 ml solution containing hexachloroplatinic acid (80 mg), scandium (III) nitrate hydrate (1.1, 2.7, and 5.2 mg corresponding to 0.2, 0.5, and 1.0 doping ratios of Sc, respectively), and nickel (II) nitrate hexahydrate (75 mg) was added drop by drop to the MoS₂@graphene dispersed solution. After mixing homogeneously, 200 μl of N₂H₄·H₂O and 300 μl of 1 M KOH were injected rapidly and stirred for 2 h and put in hydrothermal at 90 °C for 3 h. The product obtained from this reaction was centrifuged, washed using DI water and ethanol several times and dried at 70 °C for 24 h. These derived products are referred to as PtSc_{0.2}Ni/MoS₂@



Scheme 1. Preparation of the PtSc_{0.5}Ni/MoS₂@graphene anode catalysts.

graphene, PtSc_{0.5}Ni/MoS₂@graphene, and PtSc_{1.0}Ni/MoS₂@graphene, according to the amount of added scandium (III) nitrate hydrate as detailed above. The other catalysts (PtNi/MoS₂@graphene and Pt@graphene) were prepared following a similar procedure. A commercially available Pt/C (40 % Pt on Vulcan XC, Premetek) was tested here for reference. Further, PtSc_{0.5}Ni and PtNi powders were prepared and pressed in a mold at ~ 4 MPa for 2 min to form pellets with a thickness ~ 0.3 mm and ~ 5 cm² area. The ionic conductivities of the pellets in humidified hydrogen and oxygen at 80 °C were then examined.

2.2. Physiochemical and electrochemical characterizations

The X-ray diffraction (XRD) patterns of the synthesized catalysts were measured using an X-ray diffractometer (Rigaku) with Cu k_{α} source. The oxidation states of the catalysts were investigated using X-ray photoelectron spectroscopy (XPS) with K-alpha X-ray (Thermo Scientific Inc). The exact composition of the elements was examined using inductively coupled plasma mass spectroscopy (ICP-MS; Agilent, 7900). The surface morphology of the synthesized catalysts was analyzed via scanning electron microscopy (SEM; Hitachi S-4200) and transmission electron microscopy (JEOL; JEM-ARM200 F), with an energy dispersive spectrometer (EDS). The nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP- 2020 instrument with high purity nitrogen (99.99 %). The catalysts were degassed in a vacuum tube and heated at 250 °C to remove the moisture before the isotherm measurements were taken at 77.2 K.

The electrochemical measurements were carried out using a CHI 150 electrochemical workstation (China) in a three-electrode cell system, consisting of a platinum wire as a counter electrode, a Ag/AgCl reference electrode, and modified glassy carbon as a working electrode. Before starting the electrochemical experiment, the glassy carbon was first polished with alumina slurry to obtain a clean mirror finish, washed with DI water and ethanol, and dried. Next, the clean glassy carbon was coated by dropping 3 μ l of catalyst ink, which was prepared by dissolving ~ 3 mg of catalyst in 330 μ l solution containing 5 wt% Nafion (30 μ l, commercial Nafion, $\sim 5\%$ in a mixture of lower aliphatic alcohols and water) and ethanol (300 μ l) and sonicating for 15 min. The catalysts (loading ~ 6.5 μ g) in the glassy carbon electrode (area ~ 0.07 cm²) had surface area of ~ 0.928 m² g⁻¹. The electrochemical active surface areas (ECSAs) of as-prepared catalysts were determined after acid-treatment (in deoxygenated 0.5 M H₂SO₄ solution for 10 min). The cyclic voltammetry (CV) test was performed using 0.5 M H₂SO₄ both

with and without 0.5 M ethanol, with a potential range from -0.2 to +1.2 V vs. Ag/AgCl at a scan rate of 10 mV s⁻¹ under a high-purity nitrogen atmosphere (99.999%, Daesung industrial gases co. Ltd.). The CO stripping measurements were performed in 0.5 M H₂SO₄ solution. At first, CO (10 sccm, flow rate was kept) was adsorbed onto the electrodes at 20 mV for 20 min, and then the system was purged with nitrogen gas for 40 min. The electrocatalysts (at 25 °C) were subjected to two consecutive voltammetric cycles at a scan rate of 10 mV s⁻¹.

2.3. Membrane electrode assembly and electrochemical analysis

A membrane electrode assembly (MEA) with an active cell area of ~ 5 cm² (2.24 cm $\times$ 2.24 cm) was used to measure cell performance. The catalyst ink for the anode side was prepared by dispersing 200 mg of the catalyst powder in 1.9 ml of isopropanol: 5 wt% Nafion mixtures, followed by sonication for 10 min and stirring for 7 h. The catalyst ink was hand-brushed onto a carbon paper having an area of 5 cm². The catalyst loading on the carbon paper was ~ 6 mg cm⁻². A commercial Pt/C catalyst (40 wt% of Pt) was also loaded onto a carbon paper and used as the cathode. A Nafion 117 membrane (DuPont) was used as the electrolyte of the cell. For each MEA, an anode-membrane-cathode sandwich structure was prepared via hot pressing 2 MPa and 110 °C for 1 min. The MEA was inserted into graphitic plates that had a serpentine flow model for their current collector. The anode side was fed with 0.5 M H₂SO₄ solution containing different concentration of ethanol (0.5, 1.0, and 1.5 M) at a flow rate of 5 ml min⁻¹, and oxygen (200 sccm) was fed at the cathode side. Hydrogen fuel containing trace impurities of H₂S = 10 ppb, CO = 0.1 ppm are also analyzed. Single cells were further examined using methane (100 %) fuel. Biogas with a composition of CH₄ (68%), CO₂ (30%), and H₂S (2%) was also fed at 80 sccm onto the anode side of the cell, during which the open circuit voltage, current-voltage curve, and cell stability were measured. The polarization curves were measured in a fuel cell station from Carbon and Fuel Cell (CNL Energy), South Korea.

3. Results and discussion

3.1. Structure and morphology of the synthesized catalysts

The MoS₂ template prepared herein had a 3D nanoflower-like structure with nano porosity at the surface, which provides a large surface area for the electrocatalyst. Specifically, PtSc_{0.5}Ni nanoparticles

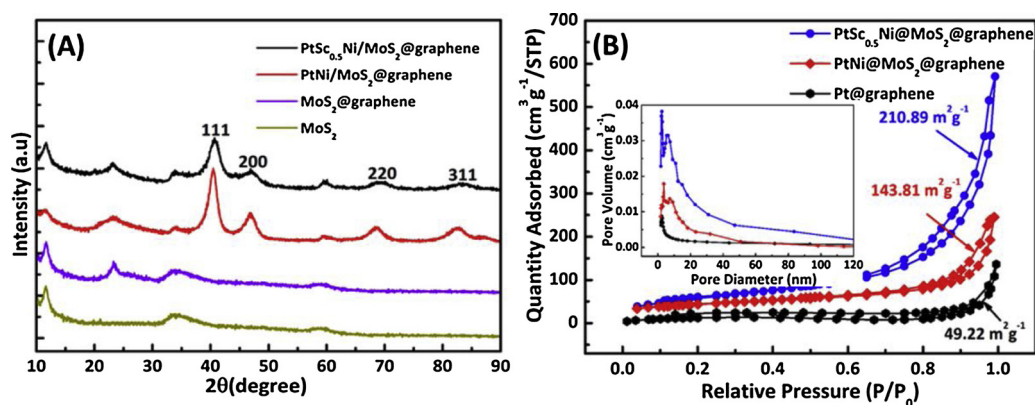


Fig. 1. (A) XRD patterns of the as-prepared catalysts. (B) N₂ adsorption-desorption isotherms and pore size distribution of the as-prepared catalysts (inset).

were formulated and grafted onto the 3D MoS₂@graphene support as an anode catalyst, as shown in Scheme 1. The powder X-ray diffraction (XRD) patterns of the synthesized catalysts are shown in Fig. 1 and Fig. S1. The 3D MoS₂@graphene shows three diffraction peaks at 13.09°, 33.41°, and 58.72°, which are assigned to the (002), (100), and (110) hexagonal phases of MoS₂, respectively [41–43]. No diffraction peaks related to impurities were observed. Furthermore, the XRD pattern of PtSc_{0.5}Ni/MoS₂@graphene catalyst shows diffraction peaks at 40.7°, 47.1°, 68.8°, and 82.6° that are respectively related to the (111), (200), (220), and (311) planes, of face-centered-cubic (fcc) structured Pt. The broad peak centered at 24.1° is related to the (002) plane of graphene.

The Pt (111) XRD diffraction peak positions are shifted slightly towards higher 2θ values compared to the standard Pt crystal (PDF No. = 04–0802) [44]. This could imply that the Sc and Ni atoms were integrated into the Pt lattice to form an alloy phase. Furthermore, peaks related to pure Pt, Sc, and Ni were not observed, while weak reflection peaks of the Sc₂O₃, Sc₂Pt₂O₄, and ScNi₂ phases were observed at 34°, 39°, and 44.5°, respectively. The lattice constants ($a^{[c]}$) and crystal sizes ($D^{[c]}$) of the nanoparticles in the catalysts were determined from the XRD analysis and listed in Table ST1. The lattice constant of the Pt nanoparticles in Pt@graphene is slightly larger (0.3967 nm) than that of the bulk Pt crystals (0.3923 nm), and this might be due to the presence of the graphene support [45,46].

After combining transition metals into Pt, the lattice constants of the Pt nanoparticles decreased to 0.3887 and 0.3754 nm in the PtNi/MoS₂@graphene and PtSc_{0.5}Ni/MoS₂@graphene catalysts, respectively which induced compressive strains on the crystal lattice. Furthermore, the lattice strain was also calculated and shown in Table ST1. The lattice strain is related to the composition, the surface oxidation states, and the sizes of the nanoparticles. The tensile strain of the Pt crystals in the Pt@graphene catalyst is 1.1%, whereas the compressive strains for the PtNi/MoS₂@graphene, PtSc_{0.2}Ni/MoS₂@graphene, PtSc_{0.5}Ni/MoS₂@graphene, and PtSc_{1.0}Ni/MoS₂@graphene catalysts are -0.9, -1.9, -4.3, and -2.67%, respectively. This indicates that PtSc_{0.5}Ni/MoS₂@graphene has less electronic band shift of Pt and possesses a lower tendency towards chemisorption than the other catalysts [15,47].

The nitrogen physisorption analysis (Fig. 1B) shows that the PtSc_{0.5}Ni/MoS₂@graphene catalyst possesses a specific surface area of 210.2 m² g⁻¹, as determined via the Brunauer–Emmett–Teller (BET) method. This value is significantly higher than those of PtSc_{1.0}Ni/MoS₂@graphene (164.38 m² g⁻¹), PtSc_{0.2}Ni/MoS₂@graphene (148.08 m² g⁻¹, Fig. S2), PtNi/MoS₂@graphene (143.81 m² g⁻¹), and Pt@graphene (49.22 m² g⁻¹) catalysts. All these catalysts possess nano or mesoporous structures. The pore volume (BJH desorption, dV/dlog D) of the PtSc_{0.5}Ni/MoS₂@graphene catalyst (0.3910 cm³ g⁻¹, with an average pore width of 15.28 nm) is much higher than those of PtNi/MoS₂@graphene (0.2705 cm³ g⁻¹, with an average pore width of 13.49 nm) and Pt@graphene (0.1711 cm³ g⁻¹, with an average pore width of 11.15 nm) catalysts. The higher specific surface area of the

first catalyst can increase the contact area at the electrode-electrolyte interface, providing more surface reaction sites and allowing faster diffusion kinetics, all of which improve the catalyst's electrochemical performance. Furthermore, from ICP-MS analysis, the elemental composition of PtSc_{0.5}Ni/MoS₂@graphene is 24.07, 0.45, 14.74, 19.30, and 4.98 wt% of Pt, Sc, Ni, Mo, and S, respectively. The obtained total mass percentage of PtScNi nanoparticles in PtSc_{0.5}Ni is 39.26%. On the other hand, the total mass percentages of PtScNi in PtSc_{0.2}Ni and PtSc_{1.0}Ni are 38.45 and 39.92%, respectively. The measurement results from ICP-MS are fairly close to the initial atomic stoichiometry. These observations might be due to better or complete chemical reduction of the precursors by the reducing agent (N₂H₄·H₂O) [48,49].

The morphology and microstructure of the as-prepared catalysts were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The small flake-shaped petals of MoS₂ nanoflower attached on the graphene surface can be clearly observed in Fig. 2A. The size of the MoS₂ nanoflower ranged from 50 to 300 nm. The presence of nano porous motif on 3D MoS₂@graphene can facilitate deposition of primary catalyst nanoparticles, which took place on the side walls of the petals and in the porous region. The higher-magnification SEM images reveal that the surfaces of MoS₂@graphene nanoflowers were well-decorated with PtSc_{0.5}Ni, PtSc_{0.2}Ni, and PtSc_{1.0}Ni nanoparticles (Fig. 2B, D and Fig. S3A, respectively). Further, in Fig. S3C, for the PtNi/MoS₂ catalyst there is no evidence of PtNi nanoparticles in some of the MoS₂ structures. This might be due to the higher saturation or agglomeration of PtNi in some particular MoS₂ structures.

The TEM images of PtSc_{0.2}Ni, PtSc_{1.0}Ni, and PtSc_{0.5}Ni nanoparticles

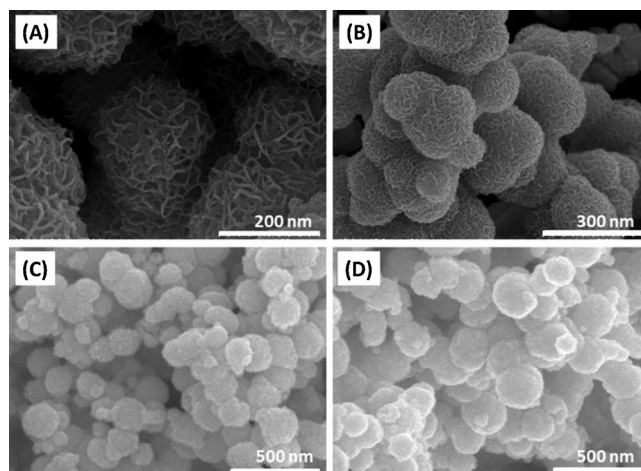


Fig. 2. SEM images of (A) MoS₂, (B,C) PtSc_{0.5}Ni/MoS₂@graphene, and (D) PtSc_{0.2}Ni/MoS₂@graphene.

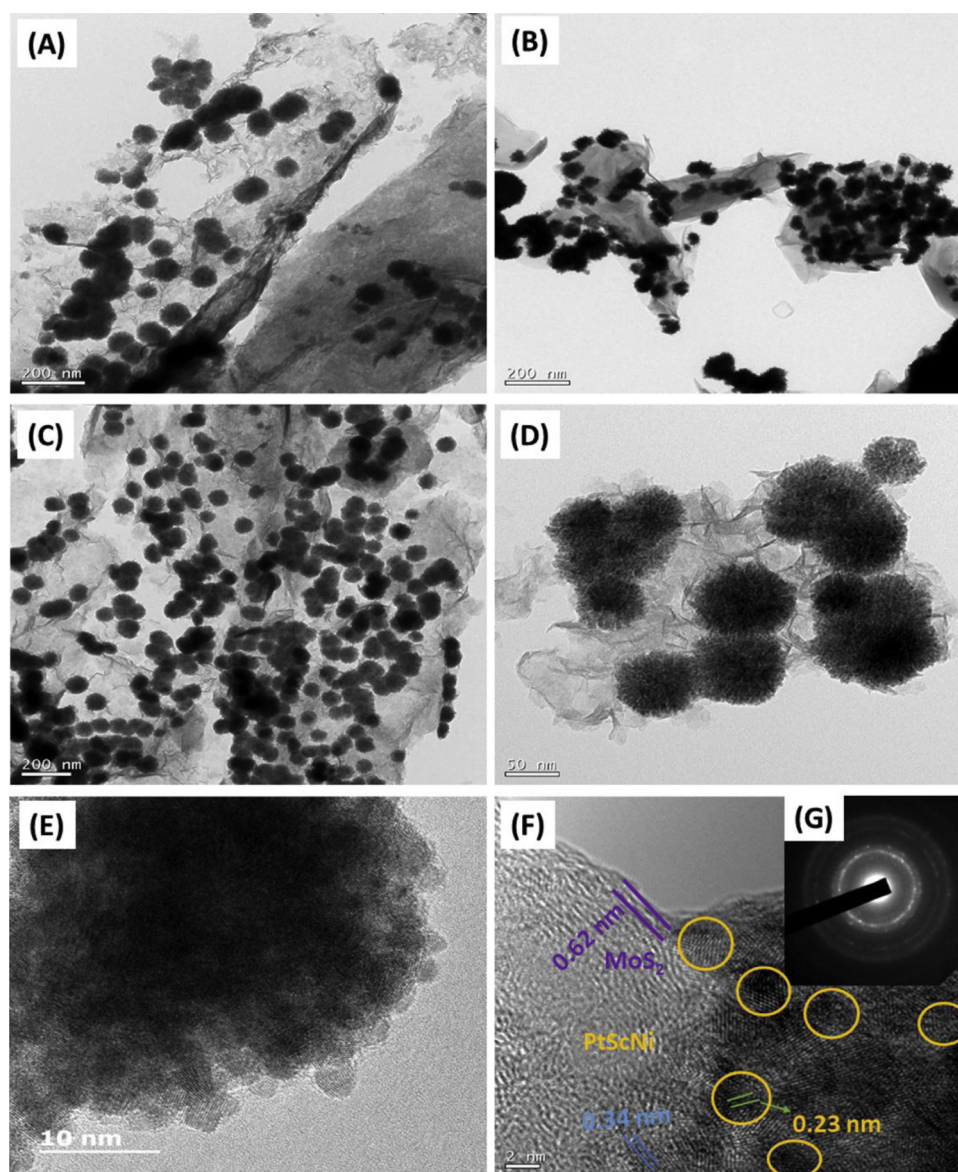


Fig. 3. TEM images of (A) PtSc_{0.2}Ni/MoS₂@graphene, (B) PtSc_{1.0}Ni/MoS₂@graphene, (C, D) PtSc_{0.5}Ni/MoS₂@graphene. (E, F) HR-TEM and (G) SAED pattern of PtSc_{0.5}Ni/MoS₂@graphene.

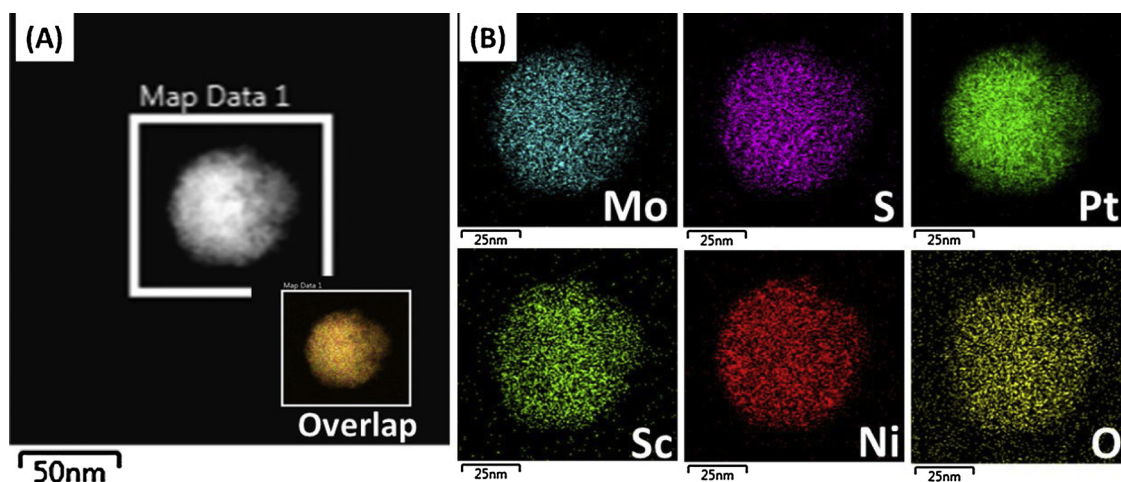


Fig. 4. HAADF-STEM image and mapping of the various elements of PtSc_{0.5}Ni/MoS₂@graphene.

are shown in Fig. 3A, B, and C, respectively. These nanoparticles are uniformly distributed across the entire surface structure of the 3D MoS₂@graphene nanoflowers. However, in PtSc_{0.5}Ni/MoS₂@graphene and PtNi/MoS₂@graphene catalysts (Fig. S4F) the nanoparticles displayed a relatively higher degree of agglomeration. To clearly identify the size of the PtSc_{0.5}Ni nanoparticles and 3D fine structure of MoS₂@graphene, HR-TEM images of PtSc_{0.5}Ni/MoS₂@graphene were evaluated. Fig. 3E and the circles marked in yellow in the Fig. 3F represent PtSc_{0.5}Ni nanoparticles, which possessed spherical structures with an average particle size of 2.2 nm. The purple lines in Fig. 3F depict the lattice fringes of MoS₂, and those with a *d*-spacing of 0.62 nm are assigned to the (002) plane of MoS₂. On the other hand, the lattice distances of 0.23 and 0.34 nm are assigned to the (111) plane of fcc PtSc_{0.5}Ni and the (002) plane of graphene, respectively. The selected area electron diffraction (SAED, Fig. 3G) pattern shows distinct diffraction rings and reveals that the PtSc_{0.5}Ni/MoS₂@graphene catalyst has a polycrystalline structure.

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive X-ray spectroscopy (EDX) elemental mapping of PtSc_{0.5}Ni/MoS₂@graphene are shown in Fig. 4. From the elemental mapping, PtSc_{0.5}Ni nanoparticles are homogeneously distributed throughout the 3D MoS₂@graphene surface (Fig. 4B), and their composition (wt%) is shown in Fig. S5. The small size of PtSc_{0.5}Ni nanoparticles can enhance their surface area and therefore the electrochemical performance. The TEM images of Pt@graphene catalysts are shown in Fig. S4G. In addition, the HAADF-STEM image and mapping of PtSc_{0.5}Ni/MoS₂@graphene catalyst also confirm the presence of Mo, S, Pt, Sc, and Ni, as shown in Fig. S6.

The activity of catalysts largely depends on the surface composition of their active components. X-ray photoelectron spectroscopy (XPS) analysis was performed to determine the electronic structures and elemental composition of the catalysts. The survey XPS spectrum (Fig. 5A) of PtSc_{0.5}Ni/MoS₂@graphene shows that its surface is composed of C, O, Pt, Sc, Ni, Mo, and S, in agreement with the elemental mapping result. The Pt 4f spectrum of the catalyst is shown in Fig. 5B. The Pt peaks located at 71.32 and 74.57 eV are assigned to 4f_{7/2} and 4f_{5/2} of metallic Pt⁰ states, respectively, showing that metallic Pt⁰ is the predominant species. Meanwhile the peaks observed at 72.84 and

77.15 eV correspond respectively to Pt²⁺ species in the forms of Pt(OH)₂ and PtO on the catalyst surface [50–52].

The Sc³⁺ (2p_{1/2}) (Fig. 5C) peaks at 407.49 and 406.53 eV are related to ScO(OH) and Sc, respectively. Sc³⁺ (2p_{3/2}), however, show peaks at 402.40 and 400.22 eV that correspond to Sc₂O₃ and Sc, respectively [19]. The Ni 2p spectrum consists of doublets of 2p_{3/2} and 2p_{1/2}, each doublet consisted of two satellite peaks following the main peaks caused by the multi-electron excitations. The peaks observed at 855.10 (Ni 2p_{3/2}), 873.19 (Ni 2p_{1/2}), 856.08 (Ni 2p_{3/2}), and 874.38 eV (Ni 2p_{1/2}) can be assigned to Ni(OH)₂ and NiOOH species (Fig. 5D) [22,47,53].

The XPS spectrum of Mo 3d shows a weak satellite peak (2s) of S species at 225.3 eV, and two peaks of Mo 3d_{3/2} (232.15 eV) and Mo 3d_{5/2} (228.77 eV) that can be ascribed to Mo⁴⁺ (Fig. 5E) [54]. The other Mo 3d_{3/2} peak observed at 235.32 eV corresponds to Mo⁶⁺, indicating that a certain degree of oxidation occurs due to the formation of MoO₃ [55]. The two main characteristic peaks of Mo 3d_{3/2} and Mo 3d_{5/2} are near the meta-stable 1T phase of MoS₂, which should improve the electrical conductivity and electrocatalytic property of the catalyst. The S 2p spectrum (Fig. 5F) consists of two main peaks located at 161.18 and 162.42 eV attributed to S 2p_{3/2} and S 2p_{1/2}, respectively; related to divalent sulfide ions (S²⁻) [56]. In addition, the small satellite peak at 163.57 eV corresponds to –C–S– ligands. The Pt 4f peaks of the PtSc_{0.5}Ni/MoS₂@graphene catalyst are shifted slightly toward higher binding energies compared to Pt/C [18]. This implies strong electronic interaction between Pt, Sc, Ni, and the support material, which can play an important role in electrocatalytic reactions. Furthermore, the surface composition values of the as prepared catalysts are shown in Table S2.

3.2. Electrochemical analysis

The electrochemical behaviors of the PtSc_{0.5}Ni/MoS₂@graphene, PtNi/MoS₂@graphene, Pt@graphene, and Pt/C catalysts were examined across a potential range of -0.2 to 1.2 V (vs. Ag/AgCl) at a scan rate of 10 mV s⁻¹ in 0.5 M H₂SO₄ solution. All the catalysts displayed hydrogen desorption/absorption and oxide formation and reduction, as shown in Fig. 6A. The ECSA was calculated using the established formula [18,57].

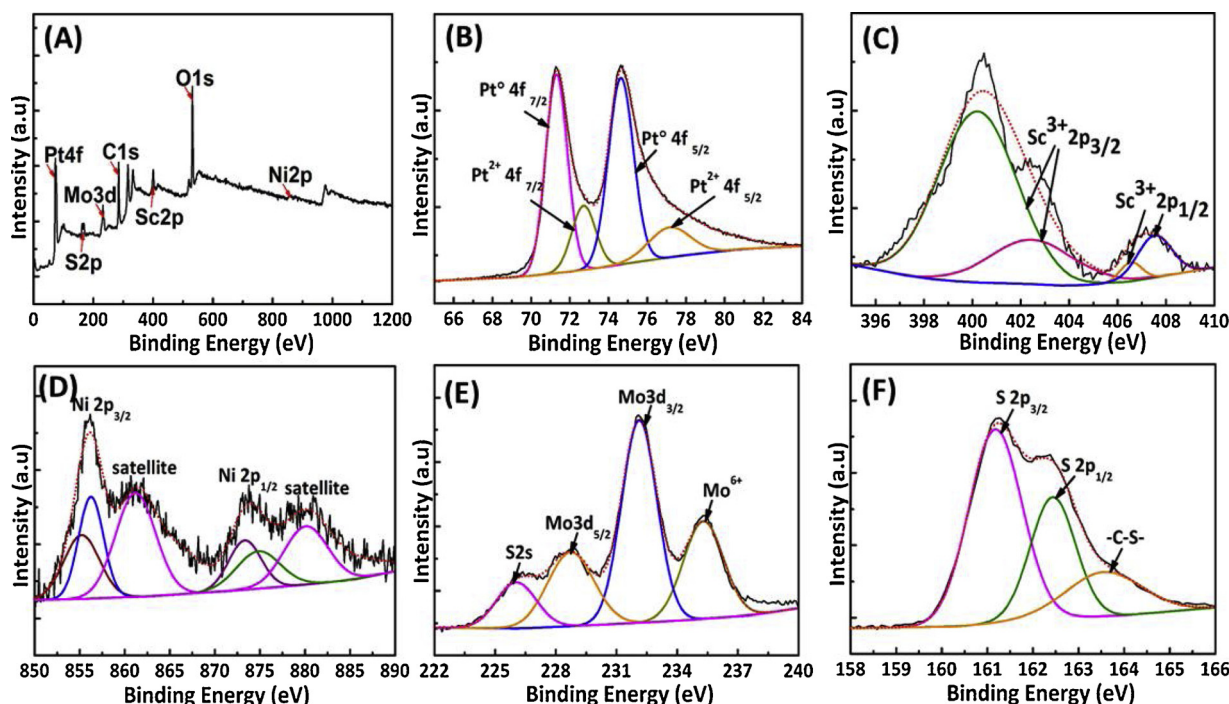


Fig. 5. XPS spectra of PtSc_{0.5}Ni/MoS₂@graphene catalyst. (A) survey scan, (B) Pt 4f, (C) Sc 2p, (D) Ni 2p, (E) Mo 3d, and (F) S 2p peaks.

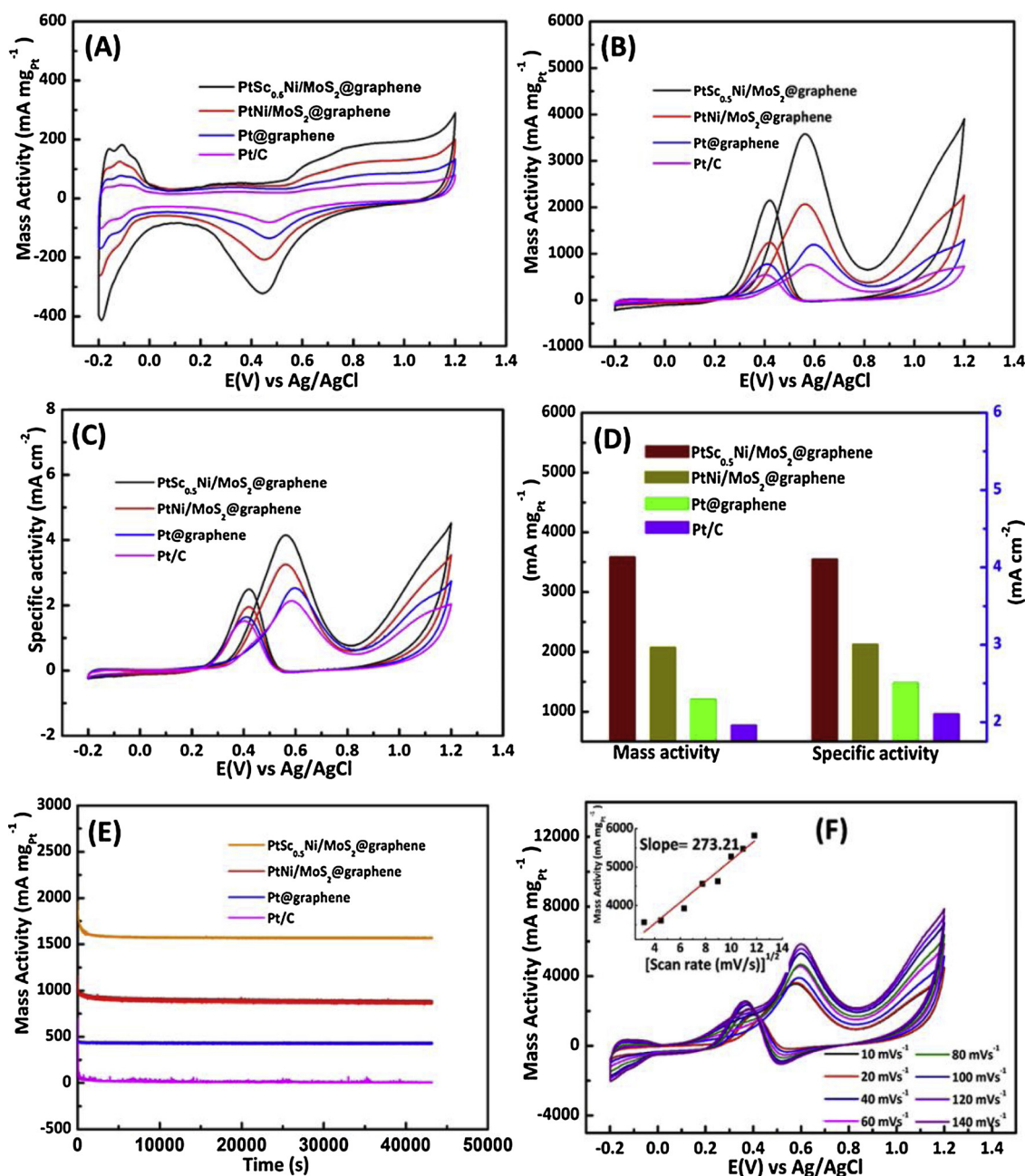


Fig. 6. Comparison of electrocatalytic performance of the PtSc_{0.5}Ni/MoS₂@graphene, PtNi/MoS₂@graphene, Pt@graphene and Pt/C catalysts. (A) CVs curves recorded in 0.5 M H₂SO₄ with a scan rate of 10 mV s⁻¹, (B) mass activity, (C) specific activity, and (D) graphical comparison of specific activity and mass activity. (E) Chronoamperometry curves recorded at 0.5 V vs. Ag/AgCl for 12 h. (F) CV curves of PtSc_{0.5}Ni/MoS₂@graphene in 0.5 M H₂SO₄ and 0.5 M ethanol at various scan rates. Inset: a plot of the current density vs. the square root of the scan rate.

$$\text{ECSA} = Q_H / [\text{Pt}] \times 0.21$$

where Q_H is the charge of H₂ adsorption/desorption and 0.21 mC cm⁻² is the charge to oxidize a single layer of a hydrogen atom on Pt surface. The ECSA value of PtSc_{0.5}Ni/MoS₂@graphene is 86.27 m² g⁻¹, which is much larger than those of the PtNi/MoS₂@graphene (63.61 m² g⁻¹), Pt@graphene (47.37 m² g⁻¹), and Pt/C (35.82 m² g⁻¹) catalysts. The larger ECSA value of the former indicates the presence of more active sites that will improve the electrochemical activity.

The electrocatalytic activities of the as-prepared catalysts towards the EOR were evaluated in 0.5 M H₂SO₄ and 0.5 M ethanol, at a scan rate of 10 mV s⁻¹, as shown in Fig. 6B. The PtSc_{0.5}Ni/MoS₂@graphene catalyst exhibited a mass activity of 3579.08 mA mg_{Pt}⁻¹, which is 1.73, 2.98, and 4.68 times higher than those of PtNi/MoS₂@graphene

(2067.59 mA mg_{Pt}⁻¹), Pt@graphene (1199.57 mA mg_{Pt}⁻¹), and Pt/C (763.95 mA mg_{Pt}⁻¹), respectively. The slower reduction kinetics of Sc³⁺ compared with Pt²⁺ can lead to good distribution of Sc atoms on the surface of the PtSc_xNi nanoparticles, and a similar characteristic was also reported for Rh atoms in PtRh bimetallic catalysts [58]. Thus, the presence of a small amount of Sc₂O₃ can significantly enhance the electrocatalytic activity of PtScNi towards EOR compared to PtNi. The specific activities of the above catalysts (Fig. 6C and Table ST3) also show a trend similar to that of the mass activities: PtSc_{0.5}Ni/MoS₂@graphene (4.1 mA cm⁻²) > PtNi/MoS₂@graphene (3.2 mA cm⁻²) > Pt@graphene (2.5 mA cm⁻²) > Pt/C (2.1 mA cm⁻²). These mass and specific activities of PtSc_{0.5}Ni/MoS₂@graphene are also higher than those reported in other studies, as summarized in Table ST4.

The presence of Sc and Sc₂O₃ nanoparticles in PtSc_xNi/MoS₂@

graphene had a positive effect on the electrocatalytic properties. As displayed in Fig. S7, the optimum catalytic activity occurs when the Sc doping ratio was 0.5. In 0.5 M H_2SO_4 and 0.5 M ethanol, the cyclic voltammetry (CV) curves displayed a peak current density of $3579.08 \text{ mA mg}_{\text{Pt}}^{-1}$ for $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$, which is much higher than those of $\text{PtSc}_{1.0}\text{Ni/MoS}_2\text{@graphene}$ ($3015.25 \text{ mA mg}_{\text{Pt}}^{-1}$) and $\text{PtSc}_{0.2}\text{Ni/MoS}_2\text{@graphene}$ ($2156.85 \text{ mA mg}_{\text{Pt}}^{-1}$). Thus, Sc_2O_3 can enhance the catalytic properties of $\text{PtSc}_x\text{Ni/MoS}_2\text{@graphene}$. On the other hand, a large amount of Sc_2O_3 can decrease the catalytic property, as Sc_2O_3 is related to higher ionic conductivity rather than electronic conductivity [19,20]. This catalytic performance agrees with the BET data mentioned earlier, which show that $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ has the highest active surface area. Hence, it is reasonable to conclude that moderate amounts of Sc and Sc_2O_3 are particularly beneficial for improving the catalytic activities.

The better electrocatalytic activity of the $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ nano-motif could be attributed to both a larger ECSA and a higher density of the active sites. Furthermore, the forward scan for the $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ catalyst exhibited a lower onset potential than those of the Pt/C catalyst. This might be due to better electronic arrangement within the nanoparticles [59]. Fig. 6D compares the mass activities and specific activities of the catalysts. Furthermore, the forward (I_f) and reverse scan (I_r) peak current densities correspond to the EOR and the chemisorbed species of EtOH_{ads} , respectively; they are unrelated to the residual carbonaceous species.

The long-term stabilities of the $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$, $\text{PtNi/MoS}_2\text{@graphene}$, Pt@graphene , and Pt/C catalysts were examined via chronoamperometry at a constant potential of 0.5 V (vs. Ag/AgCl) for 12 h in 0.5 M H_2SO_4 and 0.5 M ethanol. As shown in Fig. 6E, the oxidation current density for all catalysts decayed at the beginning. This is due to the intermediate species generated during the EOR, surface changes during cycling, or possibly the utilization of ethanol adjacent to the electrode surface [18]. The $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ catalyst shows a much slower current decay compared to the other three, confirming its excellent resistance against poisoning and better stability. Furthermore, the improved electrochemical stabilities of the as-prepared catalysts were examined for EOR using 1000 continuous cycles in 0.5 M H_2SO_4 and 0.5 M ethanol (Fig. S8). The peak current density increased initially before subsiding gradually with increasing cycle numbers. After 1000 cycles, the high mass activity of $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ led to the maintenance of 88.1% current density, which is much higher than those for $\text{PtNi/MoS}_2\text{@graphene}$ (69.1%), Pt@graphene (37.1%), and Pt/C catalysts (31.1%). Thus, the $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ catalyst exhibited better electrocatalytic performance and superior stability toward EOR, compared to the other catalysts. This might be due to the ensemble effect (better Pt atomic arrangement), bi-functional effect (the presence of Sc_2O_3 significantly improving the catalyst stability), and the strong electronic interaction between the $\text{PtSc}_{0.5}\text{Ni}$ nanoparticles and the $\text{MoS}_2\text{@graphene}$ [47].

The effect of scan rate on the catalytic EOR over $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ was also investigated (Fig. 6F). The peaks of other Pt-based catalysts are compared in Fig. S9. The forward anodic peak current increases with increasing scan rates, and this occurs alongside a positive shift in the peak potential as a result of the ohmic drop generated at high current densities. The oxidation peaks in the potential curve increase linearly with the square root of the scan rate, implying that the electrochemical ethanol oxidation on the catalyst surface is a diffusion-controlled process [18]. Moreover, the oxidation peak currents increase linearly with the logarithm of the scan rate, as shown in Fig. S10, indicating that there is a limitation in the EOR kinetics. These results suggest that the EOR is controlled by both the reaction kinetics and the diffusion process. Furthermore, $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ shows the largest logarithmic slope compared to the other catalysts, implying that it has the largest electron transfer coefficient, which is the rate-determining step.

We have further investigated the catalytic activity of the as-

prepared catalysts towards the electro-oxidation of methane and biogas containing H_2S , as shown in Fig. S11 and S12. The measurement details are included in the supporting information. The forward anodic peak at $\sim 0.38 \text{ V}$ with $168.18 \text{ mA mg}_{\text{Pt}}^{-1}$ and $\sim 0.47 \text{ V}$ with $102.38 \text{ mA mg}_{\text{Pt}}^{-1}$ current could be related to the electrooxidation of methane on the surface of $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ and $\text{PtNi/MoS}_2\text{@graphene}$ catalysts, respectively, in 0.5 M H_2SO_4 and methane. On the other hand, for Pt/C catalyst the methane oxidation peak at $\sim 0.78 \text{ V}$ along with $\sim 3.0 \text{ mA mg}_{\text{Pt}}^{-1}$ current was reported [60], which is in good agreement with pure (platinized) Pt catalyst (0.4 to 0.8 V range) in methane oxidation as hypothesized by Boyd et al. [61]. In addition, the peak current density of $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ catalyst is also higher than those of $\text{PtNi/MoS}_2\text{@graphene}$ and commercial Pt/C in 0.5 M H_2SO_4 and biogas. The CO stripping voltammograms of the electrocatalysts were obtained to analyze the CO tolerance of the electrodes. For the $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ electrode, pre-adsorbed CO was stripped from the electrode surface in the second cycle, as confirmed from the CV measurements shown in Fig. S13. For the first cycle, the oxidation peak had an onset potential of 0.08 V. $\text{PtNi/MoS}_2\text{@graphene}$, however exhibited an onset potential of 0.18 V. The lower onset potential of the former suggests that it is more active/faster at catalyzing Co_{ad} compared with $\text{PtNi/MoS}_2\text{@graphene}$. The onset potential of $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ is also lower than values from other reports [18]. This may be due to the presence of Sc that can decrease the CO adsorption strength via electronic and bi-functional effects [21]. Therefore, $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ exhibited superior CO tolerance and higher electrochemical activities than that of $\text{PtNi/MoS}_2\text{@graphene}$.

3.3. Single cells analysis

The effect of ethanol concentration (0.5–1.5 M) on the performance of a single cell consisting of $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ anode catalyst is exhibited in Fig. 7A. The peak power density increases with increasing ethanol concentration. This improvement is related to the faster ethanol transport and reaction at higher ethanol concentrations [22]. At 0.5 M, the mass transfer resistance of ethanol increases but the ethanol crossover decreases, resulting in a slightly higher open circuit voltage (OCV). Increasing the concentration of ethanol to 1.0 M decreases the mass transfer resistance, allowing more ethanol to reach the catalyst sites and therefore better catalytic performance. Further increasing the ethanol concentration to 1.5 M decreases the power density. This might be due to fuel crossover from the anode to the cathode side at higher concentrations, resulting in a mixed potential. It may also occur due to H^+ deposition over the catalyst surface [22]. In this study, the combination of 1.0 M ethanol and 0.5 M H_2SO_4 achieved the best performance for cells based on $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$. At 50°C , 1.0 M ethanol results in a maximum power density of 51.70 mW cm^{-2} , which is higher compared with those at 1.5 and 0.5 M ethanol (48.25 and 33.15 mW cm^{-2} , respectively).

The polarization curves of $\text{PtNi/MoS}_2\text{@graphene}$, Pt@graphene , and Pt/C at 50°C are shown in Fig. 7B. The fuel cell with $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ anode catalyst achieves the highest power density of 51.70 mW cm^{-2} (OCV of 0.967 V), which is approximately 1.53, 1.90, and 3.37 times higher than those of $\text{PtNi/MoS}_2\text{@graphene}$ (33.61 mW cm^{-2} , OCV of 0.94 V), Pt@graphene (15.32 mW cm^{-2} , OCV of 0.91 V), and Pt/C (9.61 mW cm^{-2} , OCV of 0.963 V) catalysts, respectively. The best cell performance for $\text{PtSc}_{0.5}\text{Ni/MoS}_2\text{@graphene}$ anode catalyst might be due to the catalyst's high surface area, uniform dispersion, the close contact of the catalyst layer with the membrane, the relatively low reactant crossover, and the mixed ion conductivity of the anode at the anode-membrane interface [2,6,19]. Dutta et al. demonstrated a novel NiPdPt/C catalyst towards EOR with a peak power density of 41 mW cm^{-2} at 40°C [62], while a maximum power density of 16.6 mW cm^{-2} at 50°C was reported for $\text{PdNi/exfoliated graphene oxide catalyst}$ [63]. Furthermore, Gerales et al. achieved a maximum power density of

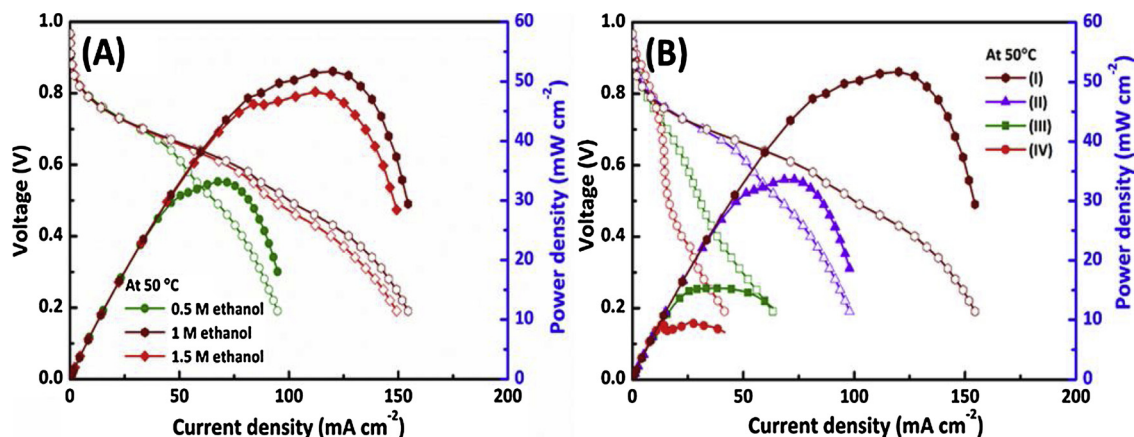


Fig. 7. Single cell performance under different ethanol concentrations. (A) Current density vs. voltage curves for ethanol concentrations of 0.5, 1.0, and 1.5 M in 0.5 M H₂SO₄, at 50 °C. (B) Influence of different anodes catalysts on the cell performance using 1 M ethanol and 0.5 M H₂SO₄ at 50 °C. (I) PtSc_{0.5}Ni/MoS₂@graphene, (II) PtNi/MoS₂@graphene, (III) Pt@graphene, and (IV) Pt/C. Cathode side: oxygen.

36 mW cm⁻² at 85 °C using PdSn/MWCNT [64].

Further, the catalysts were tested in hydrogen, methane, and biogas environments. In hydrogen fuel, a single cell with PtSc_{0.5}Ni/MoS₂@graphene exhibited the respective peak power densities of 472.34 and 898.09 mW cm⁻² at 50 and 80 °C, as shown in Fig. 8A. In comparison, single cells comprising PtSc_{0.2}Ni/MoS₂@graphene and PtNi/MoS₂@graphene anode catalysts delivered maximum power densities of 767.97 and 520.83 mW cm⁻² at 80 °C (Fig. S14). A comparative analysis of the different catalyst and their electrochemical performances is given in Table 1.

Furthermore, a single cell electrochemical test was performed to examine the feasibility of using this novel PtSc_{0.5}Ni/MoS₂@graphene catalyst for biogas containing 2% H₂S. The resultant current-voltage (I-V) curves at different operating temperatures are shown in Fig. 8B. The maximum power density increased from 12.49 to 22.75 μW cm⁻² when the operating temperature increased from 50 to 80 °C. This indicates

that a higher operating temperature can increase the ionic conductivity of the process modules and also accelerate the mass transfer of both the reactant and the product [69,70]. For comparison, at 80 °C the maximum power densities of PtSc_{0.2}Ni/MoS₂@graphene, PtSc_{1.0}Ni/MoS₂@graphene, and PtNi/MoS₂@graphene are 6.88, 11.51, and 3.74 μW cm⁻², respectively (Fig. S15).

The short-term stability of the PtSc_{0.5}Ni/MoS₂@graphene cell with a constant current density of 20 μA at 80 °C is shown in Fig. 8C. In the 1st cycle, the cell remains stable for 50 h, but a minor voltage drop occurred from 0.51 V to ~0.40 V. The drop in voltage could be related to the adsorption of gases (intermediate species such as CO and COOH) and surface passivation of the catalyst. These intermediate gas species are mediated by the surface Sc sites where they can undergo quick catalytic oxidation. Furthermore, there are two possible reasons for the sudden change or high fluctuation of voltage: (1) fuel crossover that negatively impacts the cathode by hindering oxygen accessibility to the

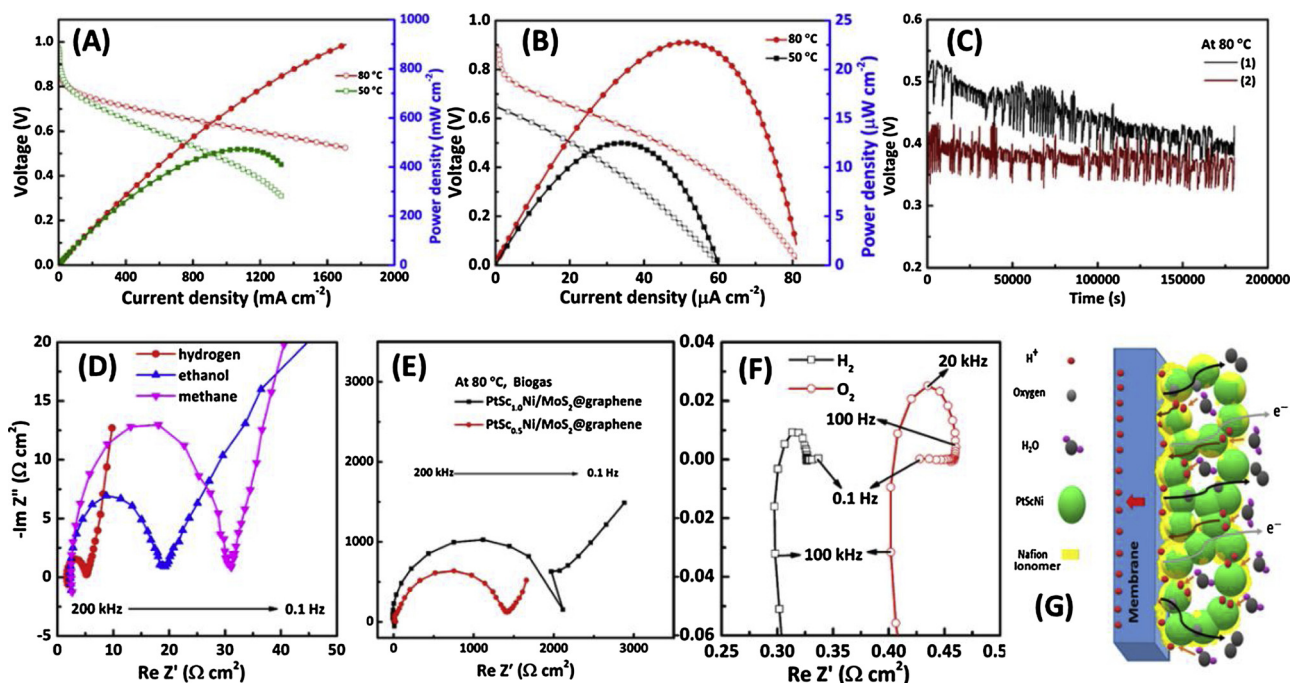


Fig. 8. Polarization curves of PtSc_{0.5}Ni/MoS₂@graphene in (A) hydrogen and (B) biogas. (C) Short-term stability test of PtSc_{0.5}Ni/MoS₂@graphene catalyst in H₂S containing biogas at 80 °C. “1” and “2” represent 1st and 2nd cycle. Impedance spectra of the unit cell consisting of PtSc_{0.5}Ni/MoS₂@graphene (D) in humidified hydrogen, methane, and ethanol at 50 °C and (E) in biogas at 80 °C. (F) Impedance spectra of PtSc_{0.5}Ni pellet (0.5 mm thickness, area 5 cm²) in humidified hydrogen and oxygen. (G) Schematic representation of the mixed ion and electron conduction in the anode.

Table 1
Performance of different catalysts using various gaseous fuels.

Anode catalysts	Membrane	Cathode catalysts	Fuels	MPD (mW cm ⁻²)	Temperature °C	Ref
AuPd/Pt	Nafion HP	Pt	H ₂	469	60	[65]
			H ₂ and 0.1% CO	~10.20	60	
Pt/C	Nafion 212	Pt ₃ Sc/CNT	H ₂	760	60	[66]
Pt-Ru/SWCNT	Nafion 117	Pt/C	H ₂	132	25	[67]
Pt/C	PBI	Pt/C	H ₂	~45	150	[68]
			C ₃ H ₈	~2.9	200	
OMC-4Bp-Pt-Cl ₂	Nafion 1110	Pt	CH ₄	~0.029	80	[39]
PtSc _{0.5} Ni/MoS ₂ @graphene	Nafion 117	Pt/C	H ₂	898.09	80	This study
			CH ₄	8.59		
			Biogas	0.0227		
PtNi/MoS ₂ @graphene	Nafion 117	Pt/C	H ₂	520.83	80	This study
			CH ₄	2.29		
			Biogas	0.0037		

*MPD = Maximum power density. *PBI = Phosphoric acid doped polybenzimidazole. *OMC = Ordered mesoporous carbon, *Bp = Bipyridyl ligand.

active sites and mixed potential [71], and (2) water flooding at the cathode site [72]. In the 2nd cycle, the initial voltage was 0.41 V and the final voltage after 50 h was ~0.38 V. Thus, this cell can effectively withstand biogas, since H₂S gas showed no adverse effect on it. To the best of our knowledge, there has been no report on low-temperature PEM fuel cells running on biogas.

The PtSc_{0.5}Ni/MoS₂@graphene, PtSc_{0.2}Ni/MoS₂@graphene, PtNi/MoS₂@graphene, and Pt/C cells were also tested in methane fuel (Fig. S16). The single cell with PtSc_{0.5}Ni/MoS₂@graphene anode exhibited ~0.81 V OCV at 80 °C and remained stable for ~83 h, as shown in Fig. S16A. Although the OCV of the Pt/C cell was measured to be ~0.72 V, it completely deteriorated in ~10 h. The PtSc_{0.5}Ni/MoS₂@graphene cell showed a maximum power density of 8.59 mW cm⁻² at 80 °C (Fig. S16B). For per mg of Pt, the power attained is 0.955 mW mg_{Pt}⁻¹, which is ~2.3 times higher compared to the value reported by Joglekar et al. (0.403 mW mg_{Pt}⁻¹) [39]. Furthermore, Nandeha et al. reported that a Pt/C catalyst using methane fuel had current and power densities of ~4.8 mA cm⁻² and ~0.37 mW cm⁻², respectively, at 80 °C [60]. On the other hand, the PtSc_{0.2}Ni/MoS₂@graphene and PtNi/MoS₂@graphene cells exhibited peak power densities of 3.63 and 2.29 mW cm⁻² at 80 °C, respectively.

Impedance spectra of the PtSc_{0.5}Ni/MoS₂@graphene cells in ethanol, humidified hydrogen, and methane at 50 °C are shown in Fig. 8D. The anodic polarization resistance of PtSc_{0.5}Ni/MoS₂@graphene in ethanol is lower compared to that in methane, because the C–H bond dissociation energy in ethanol (~423 kJ/mol at 298 K) is lower than that in methane (~439 kJ/mol at 298 K). Also, for mixed ion conducting anode catalysts, the ionic conductivity is greater in hydrous media. Further, the impedance spectra of PtSc_{0.5}Ni/MoS₂@graphene and PtSc_{1.0}Ni/MoS₂@graphene cells in biogas at 80 °C are shown in Fig. 8E. The total polarization resistance of PtSc_{1.0}Ni/MoS₂@graphene is 2114.59 Ω cm⁻², while that of PtSc_{0.5}Ni/MoS₂@graphene is 1.5 times lower (1420.0 Ω cm⁻²). One interpretation of this is that higher Sc₂O₃ can reduce the electronic conductivity and lead to poor electrochemical performances. Further, the respective polarization resistances of PtSc_{0.2}Ni/MoS₂@graphene and PtNi/MoS₂@graphene are 2671.34 and 5150.25 Ω cm⁻² (Fig. S17). The latter value is around 3.62 times higher compared with the PtSc_{0.5}Ni/MoS₂@graphene under similar conditions. Thus, mixed ion and electron conductivity may be beneficial towards achieving superior catalytic activities.

The proton and oxide conduction in the PtSc_{0.5}Ni can play a crucial role in enhancing the electrochemical activities, which was examined using PtSc_{0.5}Ni pellets as shown in Fig. 8F. The conduction of proton, oxide, and electron is schematically illustrated in Fig. 8G. Unlike PtNi, in non-mixed ion conductor catalyst, the ion conduction takes place only through the ionomer, and it is also not possible in the presence of a thin layer of ionomer on the surface of catalyst nanoparticles [73]. The

PtNi pellets did not show characteristic impedance spectra curve in humidified hydrogen and oxygen (Fig. S18), confirming the absence of ion conduction in it. On the other hand, this critical scenario is not present in mixed ion-conducting PtSc_{0.5}Ni catalyst, as the ions can be transported through the Sc₂O₃ and Sc₂NiO₄ [74]. The difference between mixed ion and non-mixed ion conducting catalysts is illustrated in Fig. S19. In mixed ion conducting anode, the ions can transfer through a shorter path, making the reaction kinetics faster and more efficient compared to the non-mixed ion conducting counterpart. Sugimoto et al. demonstrated proton and electron conduction in hydrous RuO₂ at 25 °C using impedance spectroscopy [75]. The advantages of mixed proton and electron conducting anode is well demonstrated by Rolison et al. [76]. Further, mixed ion conductivity was also illustrated for Pr₂NiO_{4+δ} anode that possessed the triple conduction of electron, proton, and oxide ions [77,78].

Overall, the outstanding performance of the PtSc_{0.5}Ni/MoS₂@graphene nanoflower catalyst can be attributed to the following advantages. (1) 3D MoS₂@graphene nanoflower serves as a support template with a large specific surface area. Furthermore, the nanoflower structure of the MoS₂@graphene support is more stable than that of non-structured MoS₂ nanoparticles [79,80]. (2) The application of highly conductive graphene improves the oxidation kinetics in various fuels. The MoS₂@graphene nanoflower support not only improves the catalytic activity, but also greatly enhances the stability of the nanoparticles and modulates the charge transfer, the local coordination environment, the density of electronic states, and the lattice strains between Pt, Sc, and Ni. (3) The presence of PtScNi alloy phase and the ionic conductivity of Sc₂O₃ improve the catalytic performance. (4) The uniform distribution of PtSc_{0.5}Ni nanoparticles on the surface of MoS₂@graphene with the same crystalline directions as the MoS₂@graphene substrate. Therefore, a strong electronic interaction with the MoS₂@graphene support occurs to prevent severe aggregation, segregation, or agglomeration of the nanoparticles. Thus, the active electrochemical surface area is significantly enhanced.

4. Conclusions

In summary, this study demonstrates a novel, economical, and simple process to fabricate hybrid PtSc_{0.5}Ni/MoS₂@graphene catalyst by using a MoS₂@graphene nanoflowers as effective template. This material exhibits improved catalytic activity and stability compared to PtNi/MoS₂@graphene and Pt/C, because of its novel morphology, composition, various effects (i.e., the strain effect, bifunctional effect, ensemble effect), and mixed ion and electronic conduction. The high activity and superior durability of PtSc_{0.5}Ni/MoS₂@graphene make it a very promising anodic catalyst for different fuel cells. Furthermore, this catalyst is not degraded in the biogas containing H₂S, thus opening a

new avenue for catalyst designing.

Authors contribution

P. Basumatary carried out the experimental work and wrote the manuscript. D. Konwar designed the catalyst, assisted in the experimental works, and revised the manuscript. Y. S. Yoon supervised the research work and monitored the project.

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.

Acknowledgements

This work was supported by the International Collaborative Energy Technology R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20158520000210). Furthermore, we would like to thank Alisha Konwar for her kind help and support during this research work.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2020.118724>.

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