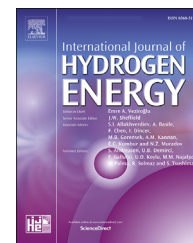


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An efficient tri-metallic anodic electrocatalyst for urea electro-oxidation

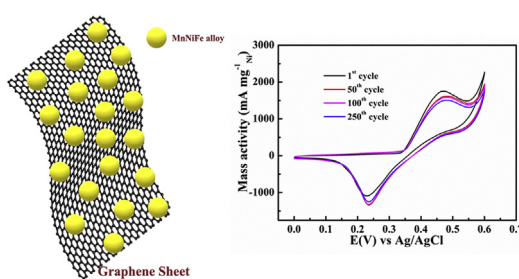
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HIGHLIGHTS

- $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ anodic catalyst was prepared by facile solvothermal method.
- Mn and Fe enhanced the defect sites of Ni and restricted the formation of γ -phase $\text{Ni}(\text{OH})_2$.
- For comparison, Ni/rGO and commercial Ni/C catalysts are also evaluated.
- The mass activity of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ was $1753.97 \text{ mA mg}^{-1}_{\text{Ni}}$.
- In DUFC, $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst exhibited a peak power density of 30.08 mW cm^{-2} at 50°C .

GRAPHICAL ABSTRACT



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ABSTRACT

Tri-metallic MnNiFe alloy nanoparticles with four different Mn:Ni:Fe weight ratios (0.5:2.0:0.5, 0.5:1.0:0.5, 1.0:1.0:1.0, and 2.0:0.5:2.0) on reduced graphene oxide (rGO) supports were synthesized using a one-pot hydrothermal method. The as-prepared catalysts were characterized by X-ray diffraction, inductively coupled plasma-mass spectroscopy, Brunauer-Emmett-Teller analysis, scanning electron microscopy, and transmission electron microscopy, and their catalytic activities were measured by cyclic voltammetry and chronoamperometry. In urea electro-oxidation, the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst exhibited superior electrocatalytic activity compared to Ni/rGO and commercial Ni/C. The $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst exhibited a mass activity of $1753.97 \text{ mA mg}^{-1}_{\text{Ni}}$, along with an onset potential of 0.34 V (vs. Ag/AgCl) in 1.0 M KOH and 0.33 M urea solution, which is ~4.2 times and 9.8 times higher than those of Ni/rGO and commercial Ni/C, respectively. Furthermore, a single cell comprising of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst exhibited a peak power density of 30.08 mW cm^{-2} in 0.33 M urea and 1.0 M KOH at 50°C .

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Introduction

The depletion of fossil fuels and rapid increase in human energy requirements have necessitated the development of high-efficiency energy generators and renewable energy devices [1,2]. Further, dependence on conventional carbon fuels alone could lead to severe issues such as global warming, respiratory diseases, and smog. Highly efficient renewable energy sources can overcome or reduce these adverse issues. Among the renewable energy generators, fuel cells can be used to efficiently produce clean energy. Urea is readily available and has a dual benefit: at first, urea can be used for low-cost hydrogen generation (water electrolysis requires 1.23 V, whereas urea electrolysis requires only 0.37 V), and secondly, it can be used as a fuel in direct urea fuel cells (DUFCs) [3]. The following reactions occur when urea is electrolyzed in alkaline media for the generation of hydrogen.

Anode: $\text{CO}(\text{NH}_2)_2 + 6\text{OH}^- \rightarrow \text{CO}_2 + \text{N}_2 + 5\text{H}_2\text{O} + 6\text{e}^-$ $E_a = -0.46 \text{ V vs SHE}$

Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ $E_c = -0.83 \text{ V vs SHE}$

Overall: $\text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{N}_2 + 3\text{H}_2$ $E^0 = 0.37 \text{ V vs SHE}$

On the other hand, urea-rich wastewater can cause both soil and environmental pollution as it can naturally go through the conversion to ammonia and carbon dioxide [4]. This exposed ammonia can pose a great danger to the ground drinking water and increase the health risk of both humans and animals. Therefore, the treatment of urea-rich wastewater can not only provide clean water but also generate electricity. Furthermore, urea is considered the most efficient indirect hydrogen carrier (have volumetric energy density of 16.9 MJ L^{-1}) because it is biodegradable, stable, non-toxic, and non-flammable [5]. In addition, it can be easily stored and transported as compared to liquid hydrogen or other volatile liquids [6]. The major obstacles to the widespread application of urea fuel cells are poor stabilities, low current densities, and slow reaction kinetics of the anodes [7].

Ni and Ni-based materials such as $\text{Ni}(\text{OH})_2$ [8,9], NiO@Ni foam [10], Ni–Mn [11], Ni–Fe [12], Ni–Co [13], and Ni–Cd [14] have been demonstrated as efficient and promising anode catalysts for the urea electro-oxidation reaction in alkaline media. However, pure or monometallic Ni suffers from high overpotential, low activity, and poor stability [12]. Therefore, combinations of Ni with different metals have been explored to achieve reduced overpotential in the urea electro-oxidation reaction, because high overpotential can lead to the oxygen evolution reaction (OER) in an alkaline medium, reducing the overall voltage efficiency and electrode stability [15]. Compared to bi-metallic alloys nanoparticles, tri-metallic alloy nanoparticles are more tunable; therefore, they exhibit superior catalytic performances and durability. Recently, nanoparticles of tri-metallic alloys such as Pt–Fe–Ni [16], Ni–Fe–Cr [17], V–Co–Fe oxide [18], and Ni–Cu–Mo [19] have been reported to exhibit good electrochemical performances in alkaline media

and suppress the OER. Thus, the tri-metallic Mn–Ni–Fe with lower overpotential is expected to suppress the OER and increase the hydrogen evolution reaction/hydrogen oxidation reaction (HER/HOR). The primary role of Mn and Fe is to prevent the formation of γ -phase $\text{Ni}(\text{OH})_2$ in alkaline media, which has lower catalytic properties compared with β -phase $\text{Ni}(\text{OH})_2$ and α - $\text{Ni}(\text{OH})_2$ [3,20]. The crystalline β -phase $\text{Ni}(\text{OH})_2$ is considered the most active phase in UOR, however β - $\text{Ni}(\text{OH})_2$ suffers from low stability in long term electrochemical reactions [21]. On the other hand, amorphous or α - $\text{Ni}(\text{OH})_2$ have exhibited remarkable electrochemical performance because of its lattice distortions, higher surface defects presence, and superior electrochemical and mechanical stability [22]. The doping of Co, Mn, and Fe to Ni-based alloy can lead to structural defects that may enhance the intrinsic activity, electronic conductivity and provide a larger active edge site for HER [23]. A direct urea fuel cell in alkaline media can generate electricity by the following reaction-

Anode: $\text{CO}(\text{NH}_2)_2 + 6\text{OH}^- \rightarrow \text{CO}_2 + \text{N}_2 + 5\text{H}_2\text{O} + 6\text{e}^-$ $E_a = -0.746 \text{ V vs SHE}$

Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ $E_c = 0.40 \text{ V vs SHE}$

Overall: $2\text{CO}(\text{NH}_2)_2 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{N}_2 + 4\text{H}_2\text{O}$ $E^0 = +1.146 \text{ V vs SHE}$

To further increase the catalytic activities and stabilities of Ni-based catalysts, they have been anchored onto conductive support materials such as carbon nanotubes, reduced graphene oxide, and carbon nanosheets. The supporting material can not only prevent agglomeration of metal nanoparticles but also increase the number of active sites. Graphene is a single layer of carbon atoms; it has garnered extensive attention because of its high electrical conductivity, excellent chemical stability, and superior electron transport properties [24,25]. Therefore, Ni-based alloy-integrated graphene expected to possess high stability and numerous electrocatalytic active sites.

Advanced designing of catalysts with a novel doping combination of transition metals with Ni is reported for DUFCs. Senthilkumar et al. and Ranjani et al. designed 3D hierarchical core-shell of $\text{Co}_3\text{O}_4@\text{NiO}$ /Carbon fiber and 3D flower-like NiCo_2O_4 /Carbon fiber anode catalysts and achieved peak power densities of 33.8 and 38 mW cm^{-2} at 60 and 80°C , respectively [15,26]. Basumatary et al. reported a peak power density of 44.36 mW cm^{-2} using Ni–Cu/ZnO@MWCNT at 50°C [20]. Li et al. prepared a CoNi/rGO@Ni (@Ni = Ni foam) catalyst and obtained a peak power density of 12.58 mW cm^{-2} at 60°C [27]. Furthermore, Tran et al. synthesized $\text{Ni}_{0.8}\text{--Co}_{0.2}(\text{OH})_2$ catalysts on the mesoporous silica template and acquired a maximum power density of 25.6 mW cm^{-2} at 70°C [28]. In this study, we have synthesized new composite catalysts with a different weight ratio of Mn:Ni:Fe/rGO by a facile and simple one-pot hydrothermal method. The as-prepared catalysts were characterized and their electrochemical properties are analyzed. The catalysts were further evaluated in a direct urea fuel cell station after preparing single cells.

Experimental section

Preparation of catalysts

First, rGO was prepared by modified Hummer's method, as described elsewhere [29]. Then, the four different wt% ratios of Mn:Ni:Fe/rGO were synthesized by a one-pot hydrothermal method. All chemicals were purchased from Sigma-Aldrich (USA). Typically, manganese (II) nitrate tetrahydrate (99%), nickel (II) nitrate hexahydrate (98.5%), and iron (III) chloride hexahydrate (98%) in the stoichiometric weight ratios 0.5:2.0:0.5, 0.5:1.0:0.5, 1.0:1.0:1.0, and 2.0:0.5:2.0, respectively, were added to 40 mL of deionized (DI) water and stirred for 5 h. Next, 30 mg of rGO and 20 mg of polyvinyl alcohol (PVA) were added to 30 mL of ethylene glycol, sonicated for 15 min, and stirred for 8 h to obtain a homogeneous dispersion. The well-mixed metal solution was then added dropwise to the rGO/PVA solution. Next, 500 μ L hydrazine monohydrate was added to the obtained aqueous solution. The resulting solution mixture was then transferred to a Teflon-vessel autoclave and heated at 160 °C for 5 h. After the hydrothermal treatment, the obtained product was washed with DI water and ethanol several times and heated in an oven at 70 °C for 12 h. The as-prepared catalysts were denoted as Mn_{0.5}Ni_{2.0}Fe_{0.5}/rGO, Mn_{0.5}Ni_{1.0}Fe_{0.5}/rGO, Mn_{1.0}Ni_{1.0}Fe_{1.0}/rGO, and Mn_{2.0}Ni_{0.5}Fe_{2.0}/rGO. In addition, Ni/rGO (40 wt% Ni) was prepared by a similar procedure, as described above. For comparison, a commercial Ni/C (40% Ni, Premetek, USA) was also evaluated.

Physiochemical and electrochemical analysis

The morphologies of the synthesized MnNiFe alloy nanoparticles on rGO supports were examined by scanning electron microscopy (SEM, Hitachi S-4200). The phase structures of the prepared catalysts were characterized by X-ray diffraction (XRD, Empyrean, Malvern Panalytical, United Kingdom) with the Cu-K α radiation ($\lambda = 0.154178$ nm). Inductively coupled plasma mass spectroscopy (ICP-MS) profiles of the catalysts were recorded using the Agilent ICP-MS 7900 system. Nitrogen adsorption and pore size measurements were performed using Micromeritics ASAP-2020. Electrochemical measurements were performed using VSP 300 Bio-Logic Science Instrument.

The catalytic activities of all the composite catalysts were measured with a three-electrode cell system using the MnNiFe/rGO (with different ratios of Mn:Ni:Fe) catalysts as the working electrodes, a Pt wire as the counter electrode, and saturated Ag/AgCl as the reference electrode. Typically, a glassy carbon electrode was polished with an alumina powder slurry, washed with DI water and ethanol, and dried in an oven. Next, the MnNiFe/rGO catalyst paste was prepared as follows: 2 mg of fine catalyst powder was dissolved in a solution of 20 μ L Nafion and 200 μ L ethanol, sonicated for 10 min, and stirred for 15 min. This procedure was followed for every catalyst paste. Afterward, 3 μ L of the prepared catalyst paste was dropped onto the glassy carbon electrode surface and dried. The loaded electrode was then used for the electrochemical analysis (under a pure N₂ atmosphere). Cyclic voltammetry (CV) was performed at the potential scan rate of

10 mV s⁻¹ in 1.0 M KOH, with and without 0.33 M urea solution. For comparison, a commercial Ni/C catalyst (40 wt% Ni) was also tested.

Fabrication of MEA and testing

At first, 60 mg of catalyst powders were put in a 10 mL solution containing an 8:2 ratio of isopropanol and Nafion. The anodic catalyst ink was hand brushed onto a carbon paper of 5 cm². The loading of the catalyst ink was ~20 mg. A commercial Pt/C (40 wt% Pt) was used for the cathode. The FAS-30 polymer membrane from Fumatech was used in single cells. The anode/membrane/cathode was sandwiched and hot-pressed at 120 °C for 1 min. The fabricated MEA (single cells) were examined in a fuel cell station (Scitech Korea Inc.). The anode was supplied with 0.33 M urea and 1.0 M KOH. The cathode side was fed with humidified oxygen. The rate of flow anolyte was 10 sccm. About 200 sccm of oxygen was supplied. (sccm = cubic centimeters per minute).

Results and discussion

Structure and morphology of the prepared catalysts

The powder XRD patterns of the as-prepared catalysts are shown in Fig. 1. The as-prepared Mn_{0.5}Ni_{2.0}Fe_{0.5}/rGO catalysts exhibited highly crystalline diffraction peaks, which were indexed to the (112), (211), (022), (202), (031), and (310) planes of the MnNiFe alloy (FeNi₃, JCPDS no: 38–0419, NiFe, JCPDS no: 18–0877, and NiMn, JCPDS no: 54–0553) with face-centered cubic structure. Small reflection peaks at 20.5°, 33.6°, and 62.5° was related to α -Ni(OH)₂ (JCPDS: 38–0715). Furthermore, no major impurity peaks were detected in the Mn_{0.5}Ni_{2.0}Fe_{0.5}/rGO catalyst. However, Mn_{0.5}Ni_{1.0}Fe_{0.5}/rGO, Mn_{1.0}Ni_{1.0}Fe_{1.0}/rGO, and Mn_{2.0}Ni_{0.5}Fe_{2.0}/rGO catalyst showed some reflection peaks at 36.0° and 61.8° that are assigned to Mn₃O₄ (JCPDS no: 13–0162, Fig. S1, supporting information). On the other hand, commercial Ni/C and Ni/rGO exhibited a simple cubic structure (JCPDS no: 04–0850) [30].

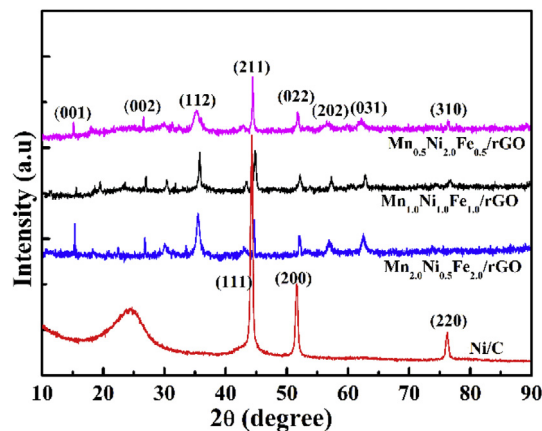


Fig. 1 – XRD patterns of Mn_{0.5}Ni_{2.0}Fe_{0.5}/rGO, Mn_{1.0}Ni_{1.0}Fe_{1.0}/rGO, and Mn_{2.0}Ni_{0.5}Fe_{2.0}/rGO catalysts.

The peaks exhibited at 15.1° and 26.5° , corresponding to the (001) and (002) planes of rGO. The average crystallite sizes of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$, and $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ were ~ 3.5 , 4.3 , and 5.6 nm respectively, as calculated from Scherrer equation [31,32]. On the other hand, the crystallite sizes of the Ni/C and Ni/rGO catalysts were ~ 4.8 nm and 4.2 nm (Fig. S1, supporting information).

According to ICP-MS analysis, the contents of Mn, Ni, and Fe in $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ were determined to be 4.70, 21.36, and 4.61 wt%, respectively. Moreover, the respective amounts of Mn, Ni, and Fe in $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ were 18.33, 4.88, and 17.95 wt% and those in $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ were 10.49, 11.73, and 9.66 wt%. The specific surface areas determined from the nitrogen adsorption isotherms (BET) for the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}$ and $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalysts were $55.92 \text{ m}^2 \text{ g}^{-1}$ and $82.11 \text{ m}^2 \text{ g}^{-1}$, respectively, as shown in Fig. S2A. The specific surface areas of $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ and $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ were $71.78 \text{ m}^2 \text{ g}^{-1}$ and $63.20 \text{ m}^2 \text{ g}^{-1}$ (Fig. S2C). The Barrett-Joyner-Halenda (BJH) desorption average pore widths of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}$ and $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ were 21.72 nm and 15.0 nm (Fig. S2B). Generally, catalysts with pore sizes of $5\text{--}15$ nm exhibit high electrochemical performances because pores in this range serve as good reaction sites and reduce the fuel and ion transport path length [33]. Therefore, $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ had a distinct advantage over $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}$ because of the rGO support.

The SEM images of the as-prepared catalysts are shown in Fig. 2. The surface morphology of $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ appeared to be rigid, and porous. A small amount of graphene stacking was found in $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ and $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$. Minor agglomeration along with miniature cluster-like formation was observed for Ni/rGO. The TEM images of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$, and $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$

catalysts are shown in Fig. 3. The $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst had spherical nanoparticles of MnNiFe alloy and average size was ~ 3.5 nm (as calculated using the ImageJ software), and the particle size distribution is shown in Fig. S3. The average particle sizes of $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ and Ni/C were ~ 5.5 and ~ 4.8 nm, respectively. Although the particle size of Ni in commercial Ni/C (Fig. S4) was smaller however the Ni particles were not uniformly distributed and covered by Vulcan carbon.

On the other hand, the alloy nanoparticles of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ were homogeneously distributed on the rGO surface with relatively uniform size. From HR-TEM (Fig. 3E) it is obvious that the doping of Mn and Fe lead to the defect sites of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$. Further, the MnNiFe alloy of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ had a d-spacing value of ~ 0.21 nm. The presence of defect sites was higher for $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ compared with $\text{Mn}_{0.5}\text{Ni}_{1.0}\text{Fe}_{0.5}/\text{rGO}$ and $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ (Fig. S5). Furthermore, the nanoparticles in $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ had some agglomeration that could negatively affect the electrocatalytic activities. The phase of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ was polycrystalline as confirmed from the selected area electron diffraction pattern (SAED), shown in Fig. 3F. The Fast Fourier Transform (FFT) displayed in Fig. 3G shows the face-centered cubic structure of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, which was also confirmed by XRD analysis.

The surface oxidation state of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst was investigated by XPS analysis. The survey spectrum (Fig. 4A) demonstrated the existence of Mn, Ni, Fe, O and C elements on the surface of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$. The high resolution Mn $2p_{3/2}$ spectra (Fig. 4B) was de-convoluted into four peaks detected at 638.9, 640.6, 642.8 and 644.9 eV, corresponding to Mn^0 , Mn^{2+} , Mn^{3+} and Mn^{4+} , respectively [34,35]. The Ni $2p$ spectra of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst (Fig. 4C) exhibit two spin-orbit doublets (Ni $2p_{3/2}$ and Ni $2p_{1/2}$) along

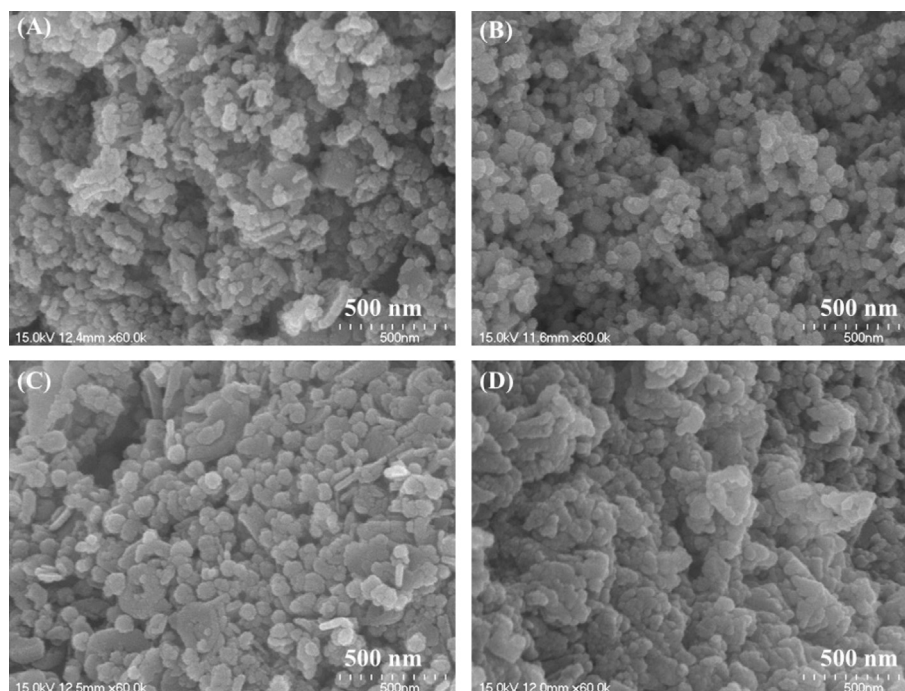


Fig. 2 – SEM images of (A) $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$, (B) $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, (C) $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$, and (D) Ni/rGO catalysts, respectively.

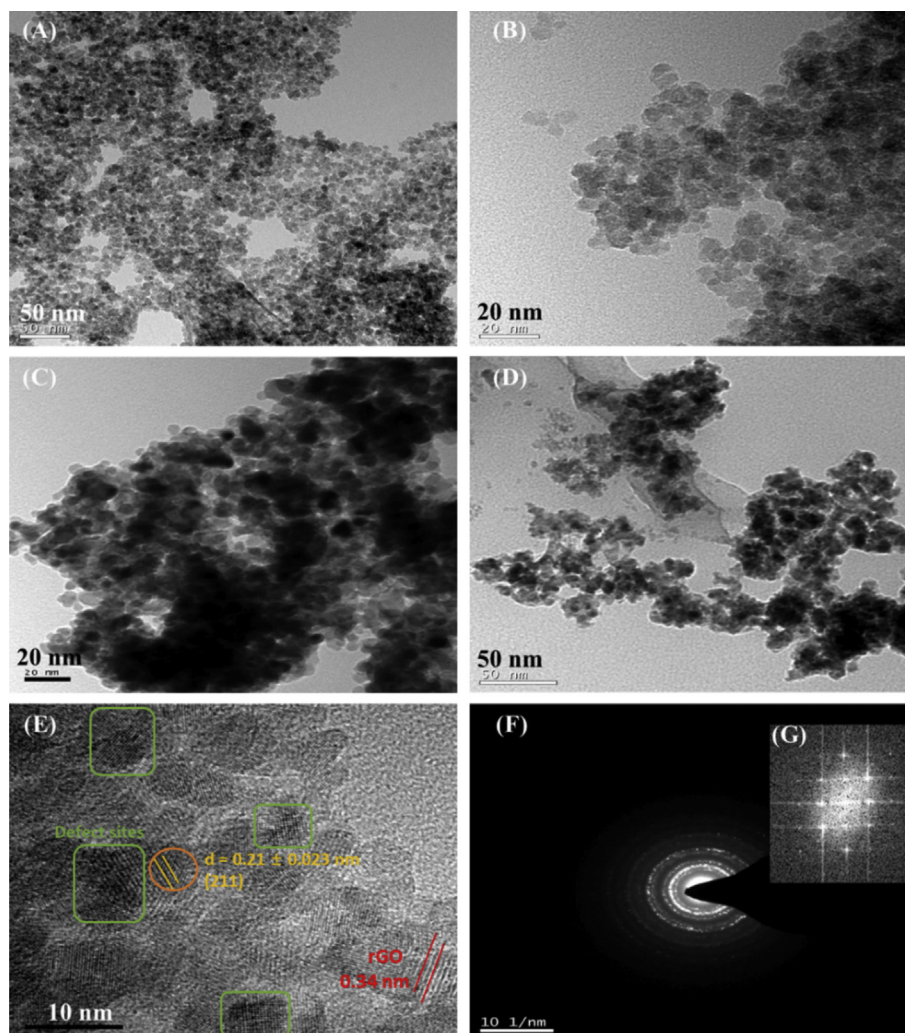


Fig. 3 – TEM images of (A,B) $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, (C) $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$, and (D) $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ catalysts, respectively. (E) HR-TEM of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$. (F) Surface SAED and (G) FFT pattern of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$.

with two satellite peaks. The peaks located at 854.9 eV ($\text{Ni } 2p_{3/2}$), 872.4 eV ($\text{Ni } 2p_{1/2}$), 856.2 eV ($\text{Ni } 2p_{3/2}$) and 874.4 eV ($\text{Ni } 2p_{1/2}$) is attributed to Ni^{2+} and Ni^{3+} species that indicates the existence of nickel hydroxide and nickel oxide on the surface of the catalyst [36–38]. The Fe 2p spectra of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ (Fig. 4D) showed peaks centered at 710.8 and 723.2 eV assigned to the binding energies (BEs) of Fe $2p_{3/2}$ and Fe $2p_{1/2}$, which indicates the Fe^{2+} formation in the catalyst surface. Additionally, other peaks located at 713.4 and 727.5 eV can be attributed to Fe^{3+} species, respectively [39,40]. The Ni 2p peaks of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ are shifted to higher binding (in contrast to the pure Ni metal 852.8 eV). The positive shift indicated that there is a strong interaction among the Mn, Ni, and Fe atoms.

Electrochemical analysis

The catalytic activities of the as-synthesized catalysts were examined by CV in 1.0 M KOH solution at the scan rate of 10 mV s^{-1} (Fig. 5A). The CV plots of the catalysts displayed two distinct redox peaks, which were assigned to anodic and cathodic transitions, respectively. The anodic peak was due to

the transformation of Ni^{2+} to Ni^{3+} and the cathodic peak was due to the reverse process. The anodic monolayer surface of $\alpha\text{-Ni}(\text{OH})_2$ has a lower electrode potential compared to $\beta\text{-Ni}(\text{OH})_2$ in alkaline media [41]. Thus, $\alpha\text{-Ni}(\text{OH})_2$ can restrict the formation of OER in alkaline media as it occurs at higher electrode potential and can enhance UOR [15]. Furthermore, Xie et al. demonstrated that Ce doped $\alpha\text{-Ni}(\text{OH})_2$ nanoarray catalyst exhibited better catalytic activities in UOR than that of Ce doped $\beta\text{-Ni}(\text{OH})_2$ [42]. The electrochemical surface areas (ECSAs) of the as-synthesized catalysts were calculated using the equation $\text{ECSA} = q_{\text{H}}/m \times q$ (for Ni, $q = 0.257 \text{ mC cm}^{-2}$) [20,43]. Notably, the ECSA of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ ($61.2 \text{ m}^2 \text{ g}^{-1}$) was considerably higher than those of $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ ($52.9 \text{ m}^2 \text{ g}^{-1}$), $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ ($43.5 \text{ m}^2 \text{ g}^{-1}$), Ni/rGO ($41.8 \text{ m}^2 \text{ g}^{-1}$), and Ni/C ($18.2 \text{ m}^2 \text{ g}^{-1}$), indicating that the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ possessed more active sites for urea oxidation.

The catalytic efficiencies of the as-synthesized catalysts for urea electro-oxidation were examined by recording CV in 1.0 M KOH and 0.33 M urea at the scan rate of 10 mV s^{-1} (Fig. 5B). $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ exhibited a mass activity of

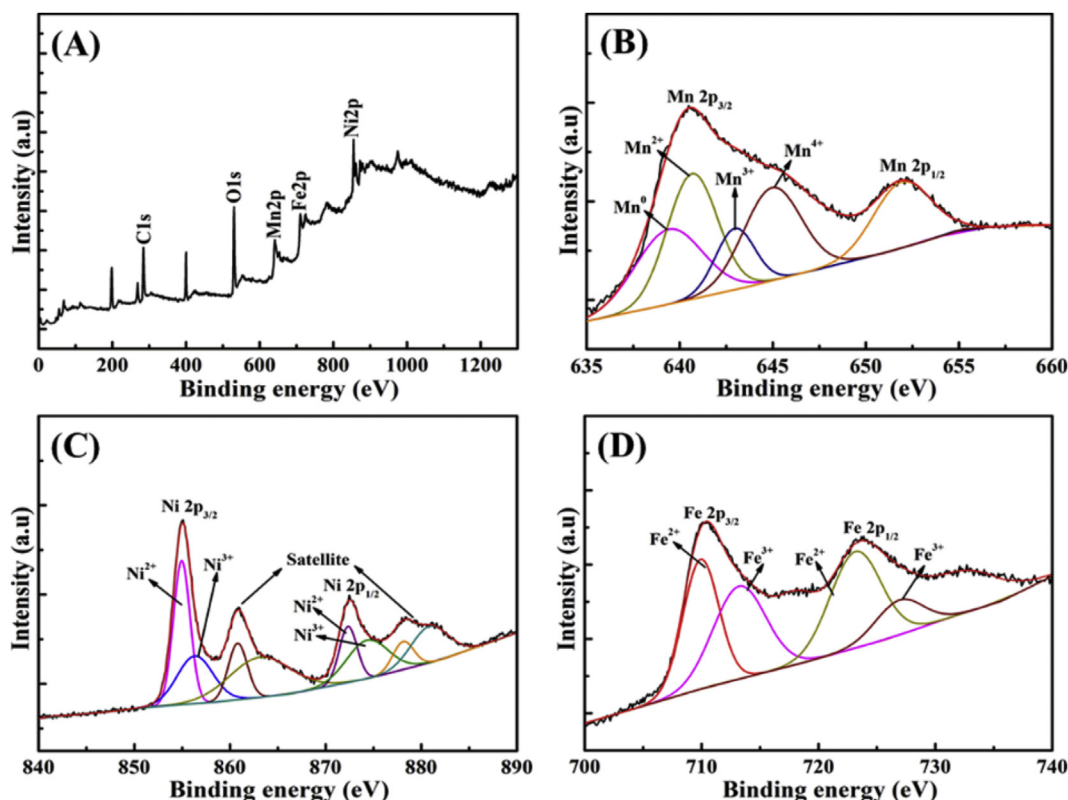


Fig. 4 – XPS spectra of (A) survey (B) Mn 2p, (C), Ni 2p and (D) Fe 2p of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst.

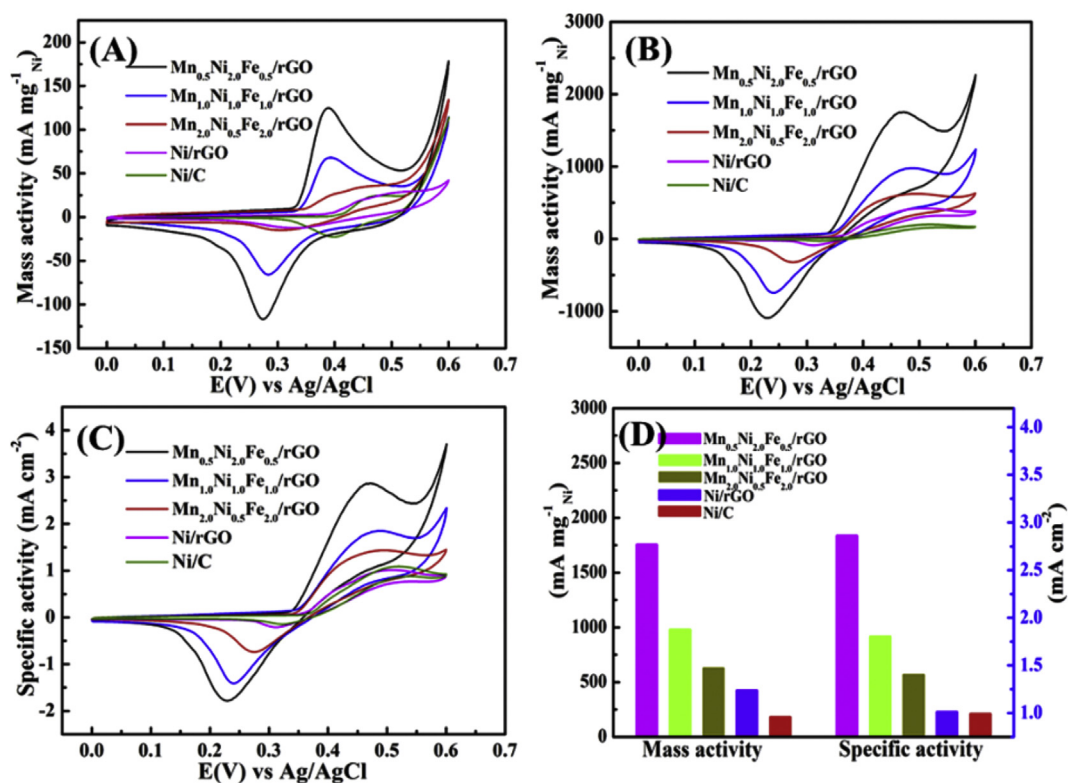


Fig. 5 – CV plots of the as-synthesized catalysts in (A) 1.0 M KOH and (B) 0.33 M urea and 1.0 M KOH solution at a scan rate of 10 mV s^{-1} . (C) Specific activity and (D) comparison of mass and specific activities.

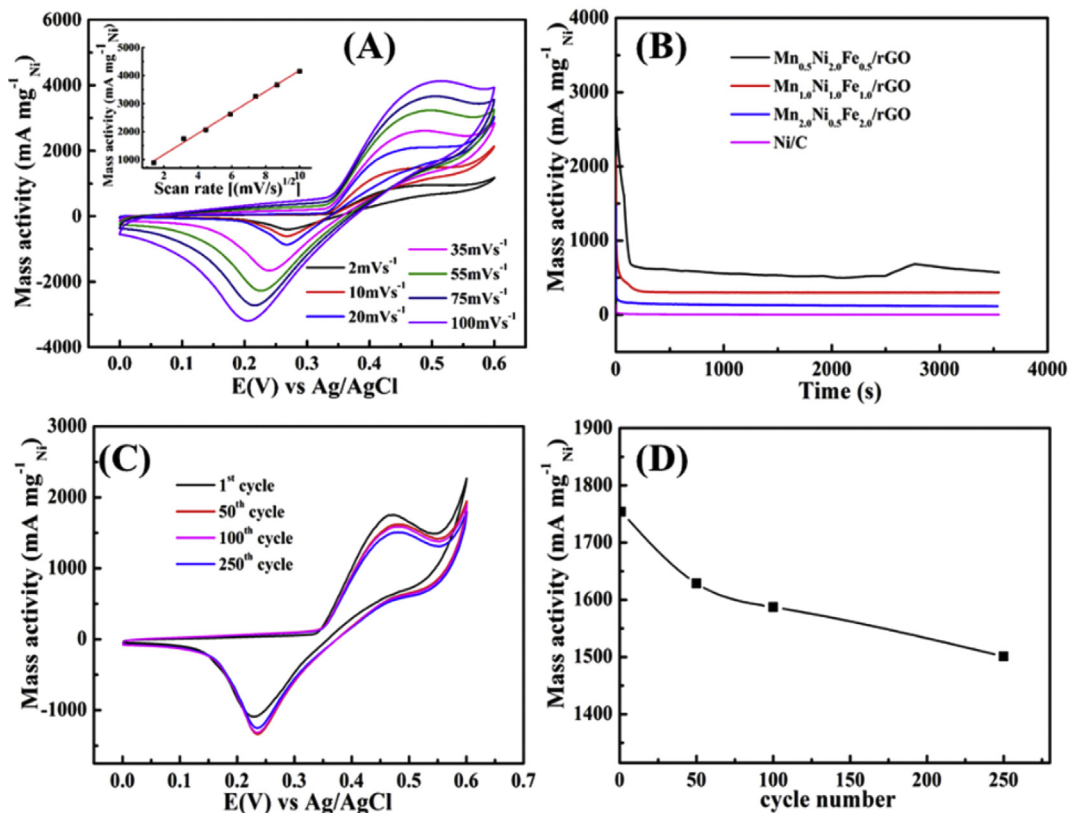


Fig. 6 – (A) CV plot of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst. Inset: plot of peak current density vs. square root of scan rate. **(B)** Chronoamperometric stabilities of all catalysts. **(C and D)** CV plots of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst for 250 cycles at 1.0 M KOH and 0.33 M urea at the scan rate of 10 mV s^{-1} .

$1753.97 \text{ mA mg}^{-1}\text{Ni}$, which was ~ 1.79 , 2.80 , 4.13 , and 9.72 times higher than those of $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ ($977.05 \text{ mA mg}^{-1}\text{Ni}$), $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ ($624.51 \text{ mA mg}^{-1}\text{Ni}$), Ni/rGO ($424.32 \text{ mA mg}^{-1}\text{Ni}$), and commercial Ni/C ($180.35 \text{ mA mg}^{-1}\text{Ni}$) catalysts. Moreover, the peak current densities for $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}$ and $\text{Mn}_{0.5}\text{Ni}_{1.0}\text{Fe}_{0.5}/\text{rGO}$ were 520.65 and $1104.62 \text{ mA mg}^{-1}\text{Ni}$, respectively (Fig. S6). These results also indicated that the supporting material (rGO) significantly contributed to electrochemical performance enhancement. The mass activity of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ was ~ 3.3 times higher than $\text{Ni}(\text{OH})_2$ nanoparticle ($530.3 \text{ mA mg}^{-1}\text{Ni}$) [44]. The linear sweep voltammetry (LSV) curves of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{0.5}\text{Ni}_{1.0}\text{Fe}_{0.5}/\text{rGO}$, Ni/rGO , and Ni/C catalyst are shown in Fig. S7. The overpotential of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{0.5}\text{Ni}_{1.0}\text{Fe}_{0.5}/\text{rGO}$, Ni/rGO , and Ni/C were 188 , 199 , 498 , and 627 mV , respectively, in 0.33 M urea and 0.1 M KOH at 25°C . Thus, the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst had lower overpotential compared with Ni/rGO and Ni/C , which is an advantage in achieving faster activation of the catalyst in UOR. Furthermore, the catalyst vs. reversible hydrogen electrode (RHE) values of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{0.5}\text{Ni}_{1.0}\text{Fe}_{0.5}/\text{rGO}$, Ni/rGO , and Ni/C catalyst were approximately -0.596 , -0.574 , -0.376 , and -0.316 V , respectively, in 0.1 M KOH and 0.33 M urea at 25°C .

The specific activities of the catalysts were calculated based on their reduction peak, along with their Ni-loading [45–47]. $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ exhibited a specific activity of 2.86 mA cm^{-2} (Fig. 5C), which was ~ 1.59 and 2.05 times higher than those of $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ (1.8 mA cm^{-2}) and $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$

(1.4 mA cm^{-2}). Moreover, the specific activity of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst was ~ 2.60 and 2.91 times higher than those of Ni/rGO (1.1 mA cm^{-2}) and Ni/C (0.98 mA cm^{-2}). The higher specific activity of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ could be attributed to the structural or electronic effects, resulting in the generation of a larger number of Ni^{3+} electroactive species [48], which promoted the oxidation of urea intermediates through bi-functional mechanisms [49]. The bifunctional mechanisms of Mn and Fe co-catalyst with Ni can be demonstrated as follows: 1) The presence of Mn and Fe can lead to fast electron transfer between support (rGO) and Ni. Further, they can restrict the growth and agglomeration of the Ni particles. While undergoing UOR on the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ surface, the electron transfers between Ni, Mn, and Fe ions and following redox reactions within the alloy can occur: $\text{Mn}^{3+} + \text{Ni}^{3+} \leftrightarrow \text{Mn}^{4+} + \text{Ni}^{2+}$ and $\text{Ni}^{3+} + \text{Fe}^{2+} \leftrightarrow \text{Ni}^{2+} + \text{Fe}^{3+}$. 2) The overpotential of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ is lowered to 189 mV from 575 mV (Ni/rGO) in 0.33 M urea and 0.1 M KOH. 3) Poisoning or deactivation of nickel is restricted/reduced by the co-catalyst Mn and Fe from the intermediate products of CO_{ads} and CO_2 .

Furthermore, smaller particle sizes with higher defect site presence of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ compared with other catalysts can be advantageous in achieving better electrochemical properties. The doping ratio of Mn and Fe in $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ may have electronic structure optimization along with surface modification. From XPS analysis the presence of Mn^0 , Mn^{2+} , Mn^{3+} , and Mn^{4+} for Mn, and Fe^{2+} and Fe^{3+} for Fe is

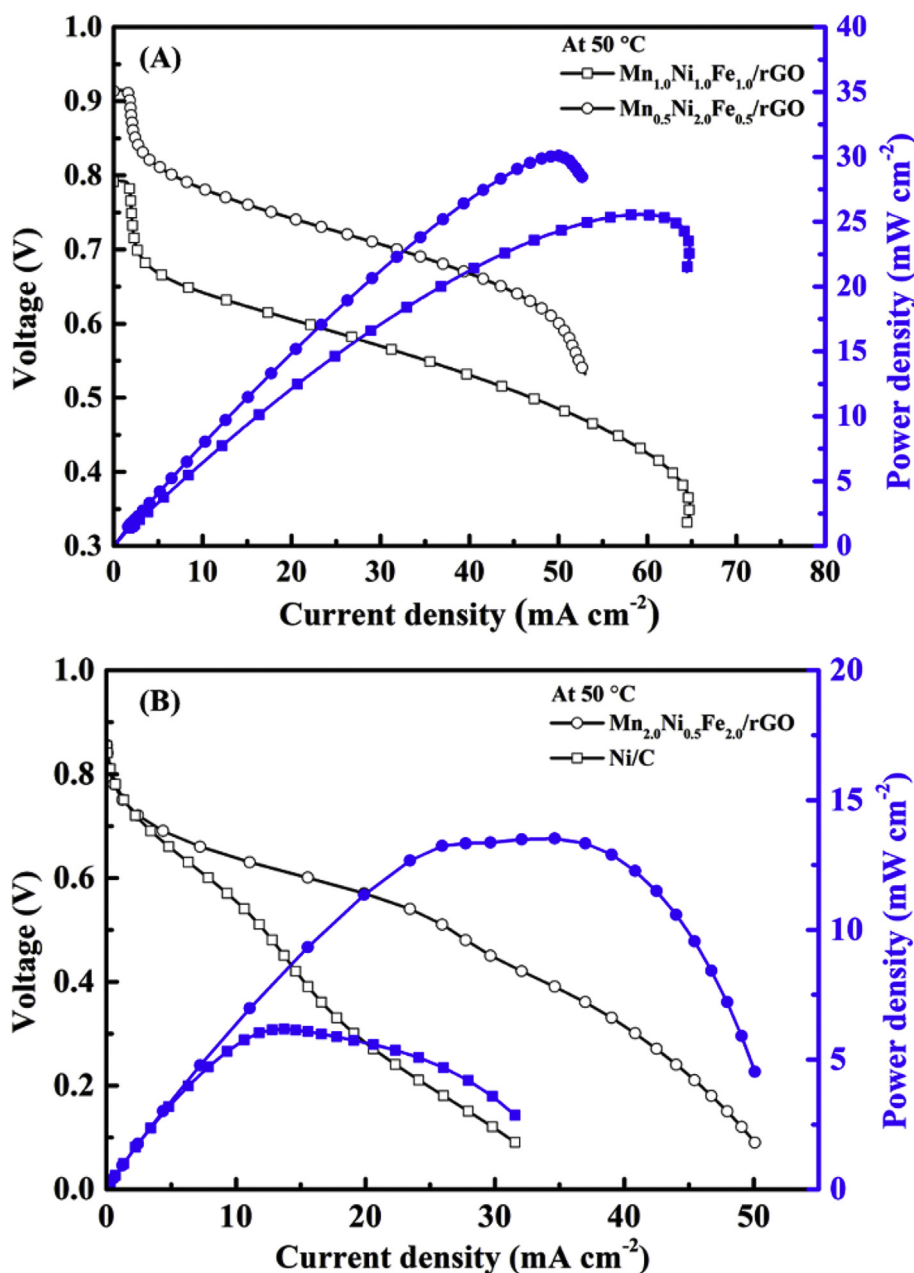
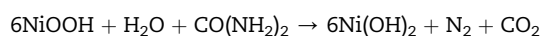
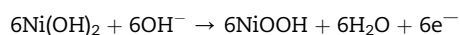


Fig. 7 – Polarization curves of single-cells of (A) $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ and $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$, (B) $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ and commercial Ni/C catalysts in 0.33 M urea and 1.0 M KOH at 50 °C.

confirmed, which can undergo redox reaction and can enhance the electrocatalytic activities by acting as co-catalyst.

The catalytic activity of a Ni-based catalyst toward urea electro-oxidation primarily depends upon the Ni active sites where the transformation of Ni^{2+}OH to Ni^{3+}OOH occurs. The oxidation of urea on the $\text{Ni}(\text{OH})_2$ surface of the catalysts could be as mentioned below and the cycle can be repeated effectively:



The higher contents of Mn and Fe in $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$ and $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ catalysts, as compared to those in $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ let to Ni-active sites reduction or blockage, resulting in a lower peak current density during urea electro-oxidation. Similar results were previously reported for Ni–Mn and Ni–Fe catalysts [11,30]. A comparison of the mass and specific activities of the prepared catalysts is presented in Fig. 5D. Importantly, the performances of catalysts prepared in this study were found to be superior to those of Ni-based catalysts previously reported [10,50–52].

The CV plots of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ at different scan rates are displayed in Fig. 6A. As shown, the forward peak oxidation current density increased with increasing scan rate. Notably,

slight positive shifts were observed for the anodic oxidation peaks. However, negative shifts were observed for the cathodic oxidation peaks, indicating quasi-reversibility of Ni^{2+} to Ni^{3+} transformation [42]. The maximum current density linearly increased with the square root of the scan rates (Fig. 6A, inset), indicating that the urea oxidation reaction occurred on the surfaces of the catalysts and it was kinetic and diffusion-controlled. It has been reported that only at urea concentrations below 0.5 M, the urea oxidation reaction becomes diffusion-controlled [11,20].

Furthermore, the electrocatalytic stabilities of the as-synthesized catalysts and commercial Ni/C were measured at 0.5 V (vs. Ag/AgCl) for 3600 s in 1.0 M KOH and 0.33 M urea solution, as displayed in Fig. 6B. Initially, the current densities rapidly decayed over time, owing to the surface changes occurring during cycling or consumption of urea adjacent to the catalyst and adsorption of unwanted species such as CO or NH_3 . The superior catalytic activities of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ alloy nanoparticles were related to higher homogeneity, larger specific surface area (as revealed by BET analysis), mesoporous structure (as confirmed by BJH calculations), and higher oxidation states of Ni (due to structural defects). The current fluctuation (increase and decrease after 2500 S) in $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalysts was related to the adsorbed gas (NH_3 and CO_2) product releasing on the surface of the catalyst [53,54].

Finally, the durability of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, Ni/rGO, and Ni/C catalyst was measured by recording CV plots for 250 cycles, as shown in Fig. 6C and Figs. S6C and D. The onset potential during the forward scan shifted in the anodic direction for all cycles with respect to the 1st cycle. The peak current remained same up to 49th cycle. However, from the 50th to 100th cycle the peak current decrease was less and not vividly distinguishable. The reduction of peak current after the 50th and 250th cycles was ~8% and ~15% (Fig. 6D), respectively, implying good durability of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst towards the urea electro-oxidation reaction. On the other hand, the reduction of peak current of Ni/rGO and Ni/C were 48% and 55%, respectively, after 250th cycle.

Furthermore, XPS analysis of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst after UOR is shown in Fig. S8. The Mn 2p peaks of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ (Fig. S8A) shifted slightly towards positive BEs and the intensities of the peaks were also decreased, this might be due to the valence redistribution (change or modification) between the Mn, Ni and Fe atoms during the electrochemical reaction. The Ni 2p peaks (Fig. S8B) also had a minor shift toward the higher BEs. The presence of Ni^{2+} was comparatively higher than Ni^{3+} before the electrochemical test but the scenario was reversed after the test. The increased Ni^{3+} content indicated that most of the nickel atoms have taken part in the redox reaction. Furthermore, the peaks (Fig. S8D) of Fe 2p were shifted slightly and the intensities of the peaks were also decreased after the UOR. This indicated that both the co-catalyst Mn and Fe were involved in achieving higher/better electrochemical activities.

The polarization curves of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$, $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$, and commercial Ni/C catalysts in 0.33 M urea and 1.0 M KOH are shown in Fig. 7. The peak power densities of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$, $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$ were 30.08, 25.51, 13.51 mW cm^{-2} ,

respectively at 50 °C. On the other hand, Ni/C exhibited a peak power density of 6.17 mW cm^{-2} , which was ~4.8 times lower than that of $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$. Anode catalyst of a ternary transition metal chalcogenide ($\text{MoS}_2\text{--NiS--Co}_3\text{S}_4/\text{rGO}$) on rGO displayed a peak power density of 21.0 mW cm^{-2} in 0.6 M urea and 1.0 M KOH [55]. On the other hand, for 0.33 M urea fuel, Yoon et al. reported a power density of 1.12 mW cm^{-2} at room temperature using the $\text{Pd}_{60}\text{Ni}_{40}/\text{C}$ catalyst [56].

Conclusions

In this study, MnNiFe alloy nanoparticles with four different Mn:Ni:Fe weight ratios on rGO supports were prepared and applied as anodic catalysts for urea electro-oxidation. Notably, the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst exhibited superior catalytic activity compared with $\text{Mn}_{0.5}\text{Ni}_{1.0}\text{Fe}_{0.5}/\text{rGO}$, $\text{Mn}_{1.0}\text{Ni}_{1.0}\text{Fe}_{1.0}/\text{rGO}$, $\text{Mn}_{2.0}\text{Ni}_{0.5}\text{Fe}_{2.0}/\text{rGO}$, Ni/rGO, and commercial Ni/C catalysts. The superior electrocatalytic activity and stability of the $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ catalyst toward urea electro-oxidation were due to better electron and ion percolation paths along with higher catalytic active sites. Therefore, $\text{Mn}_{0.5}\text{Ni}_{2.0}\text{Fe}_{0.5}/\text{rGO}$ can be potentially used as an anodic electrocatalyst in DUFCS.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2020.04.223>.

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