NiMn layered double hydroxide as efficient electrocatalyst for oxygen evolution reaction and its application in rechargeable Zn- air batteries

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NiMn Layered Double Hydroxide as Efficient Electrocatalyst for Oxygen Evolution Reaction and its Application in Rechargeable Zn-Air Batteries

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High performance catalyst for oxygen evolution reaction (OER) is in demand to improve the re-chargeability of Zn-air battery. In this work, atomically dispersed NiMn layered double hydroxides are prepared via simple hydrothermal synthesis and tested as OER catalyst in rechargeable Zn-air batteries. NiMn layered double hydroxides with the optimized Ni:Mn molar feeding ratio have good crystallinity, big interlayer spacing, and large surface area, which are beneficial to enhance their catalytic activity. They are highly active and stable during OER, showing overpotential of 0.35 V, Tafel slope of 40 mV dec⁻¹, and remarkable stability during 16 h of chronopotentiometry test. Rechargeable Zn-air batteries with NiMn layered double hydroxides as OER catalyst exhibit a low charge voltage of ≈2 V which are stable for up to 200 cycles. This study illustrates the platform to enhance catalytic activity of OER catalyst via fine-tuning the composition and physical properties of the materials and their application for rechargeable metal-air batteries.

1 Introduction

Oxygen evolution reaction (OER) is one of the key enablers of several renewable energy related applications, such as hydrogen generation via water splitting and energy storage via rechargeable metal-air batteries.¹⁻⁴ These applications promise clean and sustainable energy conversion and storage at low production cost. For example, metal-air batteries have higher theoretical energy density and better safety than most of the available battery technologies.⁴⁻⁶ In particular, Zn-air batteries which utilize an earth-abundant Zn metal anode and atmospheric O₂ cathode material have theoretical energy density of 1086 Wh kg⁻¹, more than twice of the theoretical energy density of Li-ion batteries (i.e. 460 Wh kg⁻¹).⁷⁻⁹

Nevertheless, OER requires four proton-coupled electron transfers to form oxygen-oxygen double bond. Thus, it is a kinetically and thermodynamically sluggish process which leads to high overpotential, substantial energy loss, and low efficiency of the devices.¹⁰ Subsequently, electrocatalyst is introduced to accelerate the reaction and to reduce the overpotential of OER. To date, RuO₂ and IrO₂ have been recognized as the most active OER catalyst.^{11, 12} However, the

element scarcity and high cost of these noble catalysts are impractical for their large scale applications. A number of economically attractive OER catalysts have been explored such as, transition metal oxides,² perovskites,¹ layered double hydroxides,¹³ and carbon based materials.¹⁴ Among them, Ni-based materials whose high OER catalytic activity have been rationalized via computational method are of interest due to its ubiquitous source and ease of scalability.¹⁵⁻¹⁷

NiFe and NiCo layered double hydroxides (LDH) have shown favorable OER performance in alkaline medium. The catalytic activity of NiFe LDH towards OER is particularly promising, exceeding the performance of IrO₂ and Ir/C catalysts.^{13, 18, 19} The layered double hydroxides, [M²⁺_{1-x}M³⁺_x(OH)₂][Aⁿ⁻]_{x/n}·zH₂O have unique structural property due to incorporated anions and water between the large interlayer spaces. They belong to multi-metal clay materials which consist of charged balancing anions, Aⁿ⁻ intercalated within brucite-like sheets of divalent, M²⁺ and trivalent, M³⁺ metal cations.²⁰ The composition of LDH can be easily tuned, resulting in the unique redox characteristics and notable catalytic activity during OER.^{18, 21} Diaz-Morales *et al.*¹⁵ have studied OER activity of Ni-based double hydroxide doped with various transition metals. DFT calculation suggested that doping Ni-based double hydroxides with Fe or Mn leads to an improved OER performance due to their optimum binding energy and similar active sites. However, the experimental results were not able to demonstrate the high catalytic activity of NiMn double hydroxide. Instead, it showed a much lower activity than NiFe and NiCr double hydroxides due to phase separation of Ni and MnCO₃.¹⁵

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Inspired by the above works, we prepared an atomically dispersed NiMn LDH without the need of any supporting substrates. The nanosheets of NiMn LDH with the optimized Ni:Mn molar feeding ratio shows a good crystallinity, big interlayer spacing, and large surface area. They are highly active and stable during OER, showing an overpotential of 0.35 V at 10 mA cm⁻² and Tafel slope of 40 mV dec⁻¹, which is superior than Ir/C catalyst and comparable to NiFe LDHs reported in literature.^{13, 21} Furthermore, rechargeable Zn-air batteries with NiMn LDH as OER catalyst exhibit a promising performance, showing a charge voltage of ≈2 V and good stability for up to 200 cycles.

2 Experimental

NiMn LDHs were synthesized according to our previous work with some modifications.²² In brief, Ni(NO₃)₂·6H₂O, Mn(COOH)₂·6H₂O, and 0.56 g hexamethylenetetramine (HMTA) were dissolved in 20 ml DI water. The molar feeding ratio of Ni:Mn salts were varied to the ratio of 1:1, 3:1, and 5:1 in order to achieve a total molarity of 40 mM. The solutions were hydrothermally treated in an autoclave at 80 °C for 14 h. The washed precipitates were then freeze-dried overnight to obtain NiMn LDHs. The powders of NiMn LDHs were labeled according to their Ni:Mn molar feeding ratio: Ni₁Mn₁, Ni₃Mn₁, and Ni₅Mn₁. Ni:Mn with 1:3 molar feeding ratio (Ni₁Mn₃) had also been prepared. However, brownish color impurities were observed after synthesis, which indicate the phase separation of the sample to form Mn-based compound.

Crystal structures of the samples were studied by X-ray diffractometer (Shimadzu powder diffractometer with CuKα radiation, λ=1.5406 Å). Morphologies and elemental analysis of the samples were examined by scanning electron microscopy (FESEM, JEOL 7600F), transmission electron microscopy (TEM, JEOL 2010), and energy dispersive spectroscopy (EDX) equipped in FESEM, JEOL 7600F. The surface area and pore distribution were calculated via Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, based on physical absorption of nitrogen on volumetric physisorption analyzer (Tristar II 3020).

Rotating disc electrode (RDE, diameter: 5mm) in three-electrode set-up was utilized to study catalytic activity of the samples. Catalyst ink for RDE test was prepared by dispersing 9 mg of the sample and 2.25 mg of carbon black (Vulcan XC-72) into 3 ml solution of H₂O:IPA:Nafion (ratio: 2.5:1:0.094). The ink was drop-casted onto RDE tip to attain a mass loading of 0.2 mg cm⁻². The same procedure was used to prepare commercial Ni(OH)₂ (Nacalai Tesque, Inc), RuO₂ (Sigma Aldrich), and 20 wt% Ir/C (Premetek Co) catalysts which were used as the benchmark for this study. 20 wt% RuO₂/C and 20 wt% Ni₃Mn₁/C were prepared by mixing 20 wt% of Ni₃Mn₁ or commercial RuO₂ with 80 wt% carbon black. RDE, platinum counter electrode, and Ag/AgCl (3 M KCl) reference electrode were immersed in 1 M KOH that was previously purged by O₂. Catalytic activity of the samples was investigated via cyclic

voltammetry (CV), linear sweeping voltammetry (LSV), and chronopotentiometry using a potentiostat (Autolab PGSTAT302N). CV was carried out at scan rate of 5 mV s⁻¹ and rotating speed of 1600 rpm. The samples were cycled about 5 times until a stable CV curves were obtained. LSV was performed at rotating speed of 1600 rpm. Scan rate of 5 and 0.1 mV s⁻¹ were used to obtain polarization curves and Tafel plots, respectively. 95 % iR compensation was used to correct the LSV curves before the measurements. Chronopotentiometry tests were carried out at a constant current density of 10 mA cm⁻² and rotating speed of 2500 rpm. Potential scale was calibrated to reversible hydrogen electrode (RHE). $E_{\text{RHE}} = E_{\text{Ag/AgCl(3M KCl)}} + 0.209 \text{ V} + 0.059 \text{ V} \times \text{pH}$.

Battery tests were performed in a Zn-air cell using Zn plate anode and carbon paper air cathode without any separator. The air cathode was prepared by drop casting the catalyst ink onto 2.5 × 2.5 cm² of carbon paper air cathode (10 BN SGL Carbon) to achieve a catalyst loading of ≈1 ± 0.1 mg cm⁻². Ti mesh and hydrophobic PTFE film were inserted next to the air cathode to function as current collector and waterproof backing layer, respectively. 20 ml of electrolyte (6 M KOH and 0.2 M ZnO) was then injected into the cell. The exposed area of the air cathode to the electrolyte and air is about ≈0.79 cm². Cycling test was performed using recurrent galvanostatic pulses for 10 min of discharge followed by 10 min of charge at 10 mA cm⁻² and extended cycling test for 1 h of discharge followed by 1 h of charge at 10 mA cm⁻² (battery tester, Maccor 4300).

3 Results and discussion

XRD patterns of NiMn LDHs with various molar feeding ratios are given in Fig. 1a. Each of well-defined diffraction peaks of NiMn LDHs can be indexed to series of crystal planes which correspond to hydrotalcite-like materials. The peaks are consistent with XRD patterns of NiMn LDHs reported in the literature without the presence of any impurities,^{23, 24} which indicate the successful synthesis of NiMn LDHs. Furthermore, the diffraction peaks of NiMn LDHs were shifted towards the smaller angle with the increase of Ni:Mn molar feeding ratio, suggesting the expansion of the interlayer spacing (Fig. 1b). The calculated d-spacing of plane (003) (d₀₀₃) is about 8.0, 8.2, and 8.6 Å for Ni₁Mn₁, Ni₃Mn₁, and Ni₅Mn₁, respectively. The large interlayer spacing leads to an improved OER activity due to the exposure of more active site during catalytic reaction.¹³ In addition, full width at half maximum (FWHM) of (003) peak was taken to measure the degree of crystallinity of the samples. The FWHM of Ni₁Mn₁, Ni₃Mn₁, and Ni₅Mn₁ is about 0.59, 1.41, and 1.67°, which suggest low crystallinity of the sample with high Ni content. High crystallinity of the catalyst is desirable for a robust and stable OER.^{25, 26} Thus, a balance between large interlayer spacing and good crystallinity of NiMn LDHs is needed to achieve an optimum catalytic performance during OER.

Fig. 1 (a) XRD pattern of NiMn LDHs with different molar feeding ratio of Ni and Mn salts. (b) Enlarged scale of XRD pattern of NiMn LDHs showing the peak shift of d_{003} . SEM images of (c) Ni_1Mn_1 , (d) Ni_3Mn_1 , and (e) Ni_5Mn_1 . EDS elemental mapping of (f) Ni and (g) Mn in Ni_3Mn_1 .

Ni foam is usually required as a substrate to grow Ni-based LDHs.^{14, 19, 27} In this work, hydrolysis of HMTA has been proven to favor the growth of hierarchical Ni-based LDHs without the need of any substrates. The SEM images reveal porous and interconnected nanosheets-like morphology (Fig. 1c-1e) for all samples with varied Ni to Mn ratios. These nanosheets have an open structure with minimum self-aggregation which is beneficial for the electrocatalytic reactions. Unlike high Ni content NiMn LDHs, Ni_1Mn_1 shows an aggregate of large-sized nanosheets which could lead to its limited catalytically active surface area. EDS mapping confirmed that both Ni and Mn in NiMn LDHs (e.g. Ni_3Mn_1) are homogeneously distributed throughout the sample rather than forming separate phases. These observations further support XRD results on the successful synthesis of NiMn LDHs (Fig. 1f-1g, Supplementary Information Fig. S1).

The formation of layered structure in NiMn LDHs is confirmed by TEM imaging. TEM images reveal the thin wrinkled-nanosheets that were nearly transparent to electron beams due to their ultrathin nature (Fig. 2a and Supplementary Information Fig. S2). Fig. 2b displays the discernible lattice fringes which were observed during HRTEM imaging of the Ni_3Mn_1 . A lattice spacing of 2.62 Å that corresponds to $d_{(012)}$ of NiMn LDHs are in a good agreement with XRD data. Selected area electron diffraction (SAED) pattern displays a well-defined diffraction rings, suggesting the polycrystalline nature of NiMn LDHs (Fig. 2c).

Fig. 2 (a) TEM image, (b) high resolution TEM image, and (c) selected area electron diffraction of Ni_3Mn_1 . (d) Adsorption-desorption isotherm of NiMn LDHs with different molar feeding ratio of Ni and Mn salts. Inset displays Barrett-Joyner-Halenda (BJH) plot of each sample.

SEM and TEM analysis are reinforced by the surface area and pore volume of NiMn LDHs extracted from BET measurement (Fig. 2d). Isotherm plots of NiMn LDHs with various Ni:Mn molar feeding ratios reveal the same type of hysteresis loop in the relative pressure range of $P/P_0 > 0.4$, indicating the adsorption and desorption process of porous materials. However, the high adsorbed volume of Ni_3Mn_1 indicates its larger surface area ($\approx 61.4 \text{ m}^2 \text{ g}^{-1}$) than Ni_1Mn_1 , and Ni_5Mn_1 (≈ 29.5 and $50.2 \text{ m}^2 \text{ g}^{-1}$). Surface area of $61.4 \text{ m}^2 \text{ g}^{-1}$ is higher than NiMn LDHs ($45.5 - 53 \text{ m}^2 \text{ g}^{-1}$) and NiFe LDHs ($55.1 - 60 \text{ m}^2 \text{ g}^{-1}$) reported in literature,^{14, 21, 23, 28} which suggest the advantage of tuning the amount of precursors and hydrolysis of HMTA on increasing the surface area of Ni-based LDH. In addition, most of the pores in Ni_3Mn_1 and Ni_5Mn_1 have the size of 2 to 4 nm, implying their mesoporous structure. The measured total pore volume of each sample shows similar trend to BET surface area, giving the total pore volume of 0.08, 0.16, and $0.14 \text{ cm}^3 \text{ g}^{-1}$ for Ni_1Mn_1 , Ni_3Mn_1 , and Ni_5Mn_1 , respectively. The high surface area and large pore volume of Ni_3Mn_1 indicate its favourably open structure. This characteristic will benefit its catalytic performance due to the enlarged catalytically active surface area and good accessibility of electrolyte ions.

Catalytic activity of NiMn LDHs during oxygen evolution reaction in 1 M KOH was compared to commercial Ir/C, $\text{Ni}(\text{OH})_2$, and RuO_2 catalysts (Fig. 3). Rotating disk cyclic voltammograms of all samples display sharp increase in the anodic current at potential $> 1.45 \text{ V}$, which are related to oxygen evolution reaction (Fig. 3a). The early onset and the large anodic current of Ni_3Mn_1 indicate its high catalytic

Fig. 3 (a) Cyclic voltammograms and (b) linear scan voltammograms of NiMn LDHs with different molar feeding ratio of Ni and Mn salts, commercial Ni(OH)₂, and Ir/C catalysts. The measurements were carried out at scan rate of 5 mV s⁻¹ and rotating speed of 1600 rpm in 1 M KOH. (c) Tafel plots (i.e. dash curves) showing the Tafel slope (i.e. solid curve) of the samples. (d) Stability test of Ni₃Mn₁ and Ir/C under constant current of 10 mA cm⁻² at rotating speed of 2500 rpm in 1 M KOH.

activity during OER. Unlike Ir/C and RuO₂, the voltammograms of NiMn LDHs and Ni(OH)₂ show an additional pair of redox couple, which is associated with the redox transition of Ni^{II}/Ni^{III} or IV.^{14, 18} The potentials of the redox transitions shift toward the low potential region with the increase of Mn content in the samples, suggesting the presence of Mn facilitates the redox transition of Ni. The potential for redox transition in Ni₁Mn₁ is similar to Ni₃Mn₁. However, the redox waves of Ni₃Mn₁ show an enhanced peak current which indicates more Ni participates in the redox transitions. In addition, the peak separation of Ni₃Mn₁ is smaller than that of Ni₅Mn₁ and Ni(OH)₂, implying the fast reaction kinetics of Ni₃Mn₁.

Catalytic activity of the samples was further quantified by linear sweep voltammetry (LSV). LSV curve records the required potential above the standard reaction potential (i.e. overpotential) to achieve certain current density during OER (Fig. 3b). The onset of OER in Ni₃Mn₁ was observed at overpotential of 0.26 V and it needs overpotential of 0.35 V to achieve current density of 10 mA cm⁻², 30 mV higher than overpotential of RuO₂ (0.32 V). Ir/C and Ni₅Mn₁ have similar overpotential at 10 mA cm⁻², showing overpotential of ≈0.39 V. On the contrary, LSV curves of Ni₁Mn₁ and Ni(OH)₂ exhibit a weak current density within the tested potential range. High overpotential is needed by Ni₁Mn₁ and Ni(OH)₂ catalysts to achieve current density of 10 mA cm⁻² (≈0.42 and 0.44 V), indicating their low catalytic activity towards OER. In order to have a better comparison to Ir/C which only contains 20 wt% Ir, LSV curves of 20 wt% RuO₂/C and 20 wt% Ni₃Mn₁ were also measured (Supplementary Information Fig. S4). With 80 wt%

of carbon black, the overpotential of RuO₂ and Ni₃Mn₁ are 0.37 and 0.38 V, respectively.

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Tafel plots derived from LSV curve of each sample are constructed to gain more insight into OER activity (Fig. 3c). Tafel slopes of the linear region near OER onset potential of Ni₃Mn₁ and Ni₅Mn₁ were about the same (≈40 mV dec⁻¹), lower than Tafel slope of RuO₂ (≈49 mV dec⁻¹), Ni₁Mn₁ (≈41 mV dec⁻¹), Ir/C (≈44 mV dec⁻¹), and Ni(OH)₂ (≈67 mV dec⁻¹). The fast increase of anodic current during OER results in the lower Tafel slope of NiMn LDHs as compared to RuO₂ and Ir/C (Fig. 3a). The low Tafel slope of NiMn LDHs indicates the acceleration of electron transfer/migration during the catalytic process, leading to the superior OER performance of NiMn LDHs.

The long term durability of OER catalyst is a crucial factor for its practical application. The stability of Ni₃Mn₁ and Ir/C were tested at constant current density of 10 mA cm⁻². The measured potential of both samples during the stability test are given in Fig. 3d. Ni₃Mn₁ exhibits a stable potential over 16 h of the durability test, with only a minor change from 1.60 to 1.66 V. On the contrary, the potential of Ir/C continues to increase from 1.65 to 1.73 V in the first 6 h of testing, suggesting significant activity loss of the catalyst before it completely degraded after 7.6 h of testing. It is worth noting that stability test was conducted at fast rotation speed of 2500 rpm to facilitate the diffusion of the evolved O₂ gas at the surface of the electrode. Despite that, delay in the removal of O₂ gas from the surface of the electrode caused the fluctuation of the measured potential at about ±0.015 V during the first 8 h of the measurements. Similar observation was also reported by Jia *et al.*²⁹ During the prolonged stability test, O₂ bubble continued to accumulate and blocked the access of electrolyte onto the catalyst, causing an increase of the potential. The potential recovered to its original value, once the bubbles detach from the electrode surface and diffuse into the electrolyte. We have also carried out the stability test for RuO₂ catalyst. Due to the low overpotential of RuO₂ at 10 mA cm⁻², O₂ gas generated at the surface of RDE glassy carbon is considerably high, causing significant fluctuation in the measured potential (Supplementary Information Fig. S5).

In terms of OER activity, an overpotential of 0.35 V and a Tafel slope of 40 mV dec⁻¹ made NiMn LDHs comparable to NiFe and NiCo LDHs reported in literature.^{13, 18, 21, 27, 30} Although some works have reported the improved overpotential (< 0.3 V), the tests were conducted in a conventional three-electrode test by using highly porous and conductive substrates (e.g. Ni foam and carbon paper).^{14, 19, 31} In comparison to IrO₂ which is an advisable reference catalyst instead of Ir/C, NiMn LDH has an improved stability and lower Tafel slope by compromising only ≈12 mV of its overpotential.^{13, 32, 33} Furthermore, the overpotential of our NiMn LDHs catalyst is as small as that of the recently reported NiMn LDH/MWCNT (≈0.35 V). The high performance these NiMn LDHs, despite the absence of a highly conductive MWCNT matrix, is likely benefitted from its large interlayer spacing.²⁹ Other similar approaches to lower the

Fig. 4 (a) Stability of Zn-air batteries with Ni_3Mn_1 , commercial RuO_2/C , and Ir/C catalyst during extended cycling test at discharge/charge current of 10 mA cm^{-2} for 2 h per cycle. Cycling stability of Zn-air batteries with (b) Ni_3Mn_1 and (c) Ir/C catalyst during pulse cycling test at discharge/charge current of 10 mA cm^{-2} for 20 min per cycle. Discharge and charge curve of Zn-air batteries with (d) Ni_3Mn_1 LDH and (e) Ir/C catalyst during selected cycles of the pulse cycling test.

overpotential includes the incorporation of graphene into Ni-based LDHs.^{14, 34} However, these approaches are disadvantageous for the long term stability of OER catalyst in alkaline electrolyte, as the oxidation of carbon in alkaline electrolyte during OER may lead to the low stability of the catalyst. Importantly, without the need of CNTs or graphene additives, the catalyst Ni_3Mn_1 exhibits an excellent OER stability as compared to that of the composites of Ni-based LDH/carbon based materials reported in the literature.^{14, 29, 30, 34}

The potential application of NiMn LDHs as OER catalyst was demonstrated in rechargeable Zn-air batteries. A catalyst is needed to tackle the sluggish kinetics of OER during charging of Zn-air battery. An effective OER catalyst results in the low charging voltage and stable performance of the battery. In addition to the desirable crystallinity, the enhanced porous structure of Ni_3Mn_1 facilitates the facile three-phase reaction of the catalyst, oxygen, and electrolyte, leading to the high utilization of active materials.³⁵ Catalyst ink consisting of active materials, carbon black, and binder were coated on the carbon paper and used as air cathode in rechargeable Zn-air batteries. The stability of Zn-air batteries with Ni_3Mn_1 , RuO_2/C , and Ir/C catalysts during the extended cycling tests for 2 h per cycle are given in Fig. 4a, showing an enhanced stability of the batteries with Ni_3Mn_1 catalyst as compared to the batteries with Ir/C and RuO_2/C catalysts. The pulse cycling test was carried out to further validate the durability of Zn-air batteries with NiMn LDH catalyst. The stability and voltage profile of Zn-air batteries with Ni_3Mn_1 and Ir/C catalysts during the pulse cycling tests are given in Fig. 4b-e. The initial charging voltage

of Zn-air battery with Ni_3Mn_1 catalyst shows a voltage of $\approx 1.98 \text{ V}$ which is lower than that of the battery with Ir/C catalyst ($\approx 2.02 \text{ V}$). Moreover, the battery with Ni_3Mn_1 maintains a relatively stable charging voltage for about 200 cycles of cycling test (Fig. 4b and 4d). The change of charging voltage over 200 cycles was only about 0.11 V (1.98 to 2.09 V), which correspond to a degradation rate of 0.55 mV (or 0.028%) per cycle. In sharp contrast, the charging voltage of the battery with Ir/C catalyst gradually increases to 2.13 V in the first 75 cycles, giving a degradation rate of 1.47 mV (or 0.073%) per cycle (Fig. 4c and 4e). An even worse scenario was that the Ir/C based batteries suffered drastic performance degradation after merely 80 cycles, where the discharge voltage dropped close to 0 within 5 minutes. This is far worse as compared to the performance of Ni_3Mn_1 based batteries in the 300th cycle (Fig. 4c). The lower charging voltage as well as slower degradation rate of the battery with Ni_3Mn_1 catalyst as compared to the literature³⁶⁻³⁹ and to the battery with Ir/C catalyst echo the improved OER catalytic performance of Ni_3Mn_1 revealed by RDE studies.

The discharge voltage of Zn-air batteries is normally governed by the activity of catalyst towards oxygen reduction reaction (ORR) and the conductivity of electrode.^{40, 41} Despite the use of conventional carbon black as the main ORR catalyst, Zn-air battery with Ni_3Mn_1 as OER catalyst has demonstrated an enhanced stability as compared to the rechargeable Zn-air batteries in the literature,⁴²⁻⁴⁵ which is likely attributed to the high OER catalytic activity and stability of Ni_3Mn_1 . Moreover, high performance OER catalyst enables charging at lower potential which reduces the corrosion of carbon-based air cathode in alkaline electrolyte and improves the stability of rechargeable Zn-air battery, subsequently. This is further supported by the poor stability of Zn-air battery with Ir/C catalyst which shows an early degradation in the discharge voltage as compared to the battery with Ni_3Mn_1 catalyst (Fig. 4c). Degradation in the discharge voltage is related to the loss of catalytic activity in ORR catalyst (e.g. carbon). Low activity of Ir/C catalyst leads to high charging voltage of the battery which degrades ORR catalyst, resulting in the low stability of rechargeable Zn-air battery.

4 Conclusions

The synthesis of NiMn LDHs and their application in rechargeable Zn-air batteries have been reported. Material characterizations and RDE studies reveal the effects of the composition and physical properties of the materials on their catalytic activity. Large surface area and desirable degree of crystallinity are beneficial for the fast kinetics of catalytic reaction during OER. In this case, the optimized atomically dispersed NiMn LDHs with 3:1 (Ni:Mn) molar feeding ratio exhibit high degree of crystallinity, big interlayer spacing, large surface area, and highly porous structure. They are highly active and stable during OER, showing overpotential of 0.35 V , Tafel slope of 40 mV dec^{-1} , and remarkable stability during the durability test. Furthermore, rechargeable Zn-air batteries with

NiMn LDHs as OER catalyst is firstly demonstrated, showing a low charging voltage of ≈ 2 V and stable performance for up to 200 cycles. This work contributes to the advancement of synthesizing high performance OER catalyst in order to improve the re-chargeability and stability of Zn-air batteries.

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