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Mesoporous Ternary Nitrides of Earth-Abundant Metals as Oxygen Evolution Electrocatalyst

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HIGHLIGHTS

• 3D mesoporous Ni₃FeN was constructed through hard templating and thermal nitridation.
• Ni₃FeN exhibits superior electrochemical performance for OER with a small overpotential of 259 mV to achieve a 10 mA cm⁻².
• Ni₃FeN can also deliver a lower charging voltage and longer lifetime than RuO₂ in a rechargeable Zn–air battery.

ABSTRACT As sustainable energy becomes a major concern for modern society, renewable and clean energy systems need highly active, stable, and low-cost catalysts for the oxygen evolution reaction (OER). Mesoporous materials offer an attractive route for generating efficient electrocatalysts with high mass transport capabilities. Herein, we report an efficient hard templating pathway to design and synthesize three-dimensional (3-D) mesoporous ternary nickel iron nitride (Ni₃FeN). The as-synthesized electrocatalyst shows good OER performance in an alkaline solution with low overpotential (259 mV) and a small Tafel slope (54 mV dec⁻¹), giving superior performance to IrO₂ and RuO₂ catalysts. The highly active contact area, the hierarchical porosity, and the synergistic effect of bimetal atoms contributed to the improved electrocatalytic performance toward OER. In a practical rechargeable Zn–air battery, mesoporous Ni₃FeN is also shown to deliver a lower charging voltage and longer lifetime than RuO₂. This work opens up a new promising approach to synthesize active OER electrocatalysts for energy-related devices.

KEYWORDS Ordered mesoporous structure; Hard template; Ni₃FeN; Oxygen evolution reaction; Zn–air battery
1 Introduction

Among the electrochemical processes, the electrocatalytic oxygen evolution reaction (OER) has considerable scientific and economic advantages for energy conversion and storage applications, such as water splitting or metal–air batteries [1, 2]. Particularly, the small overpotentials and fast kinetics required for catalyzing OER make it potentially cost-effective. Using precious metal catalysts ruthenium (Ru) and iridium (Ir) oxides, the potential of this technology has been proved with excellent electrocatalytic characteristics [3, 4]. However, these noble metal-based catalysts are impractical due to their rarity and high cost, limiting their widespread use [5]. To address this concern, efforts have been made toward developing earth-abundant low-cost and highly active OER electrode materials, such as metal-perovskite oxides [6], sulfides [7], nitrides [8], and phosphides [9]. Among them, transition metal nitrides (TMNs) have emerged as promising low-cost alternatives due to their rapid electron transport properties and excellent chemical stability [10].

A significant decrease in overpotential can be achieved through various approaches to optimize the surface nanostructure and electronic states for OER electrocatalysts [11, 12]. One approach, the introduction of an additional transition metal element, allows tuning of the electronic structure and improvement of the precipitation energies compared to single-metal materials [13] due to the synergistic effect of a mixed metal system. For example, the incorporation of Fe into CoN has been shown to improve the catalytic performance compared to pure cobalt nitride [14, 15]. As another approach, the formation of nanostructured TMNs can provide abundant accessible active sites, high infiltration capacity, and large contact area [16]. By combining these two approaches, three-dimensional ordered mesoporous mixed metal nitrides could be made with uniform mesochannels, large surface areas and pore volume, and high electron conductivity. However, they would only be of practical interest in OER electrocatalysis [17, 18]. There has been some success in producing mixed metal transition metal nitrides by, for example, heating the respective oxide precursor under ammonia [14, 16], plasma-based nitridation [19], or in situ nitridation of metals supported on nitrogen-doped carbon [20]. However, there remain significant technical difficulties and fundamental challenges in synthesizing ordered nanostructured materials using these approaches.

Nanocasting synthesis using mesoporous silica as a hard template has attracted tremendous interest as a platform for developing efficient electrocatalysts based on earth-abundant metals [21]. The hard templating route has been successfully developed to prepare high-surface-area mesoporous multi-metal materials for OER from mixed oxides [22], perovskites [23], and phosphides [24]. Various synthesis routes for ordered mesoporous transition metal nitrides by nanocasting have also been developed [25]. This generally takes one of two synthetic routes: direct nitridation of mesoporous oxides or the transformation of mesostructured metal oxides/silica composites to nitrides/silica composites. Though there has been some success with mixed metal materials, to the best of our knowledge, mixed metal nitrides have not been significantly developed. By combining the benefits of nanocasting, with the synergetic effects of the electronic structure derived from multi-metal nitrides, one can achieve highly efficient mesoporous OER electrodes from a facile approach to achieve high catalyst loading.

Herein, we developed a facile two-step nanocasting–nitridation strategy to achieve a bimetal nitride Ni3FeN with ordered mesoporous structures, uniform mesopores, large pore volume, and large surface areas. Benefiting from both high catalyst loading and large contact area between the catalyst and electrolytes, this mesoporous Ni3FeN catalyst exhibits highly efficient and stable catalytic activity toward the OER in an alkaline solution. It exhibits a very low overpotential (259 mV) to achieve a 10-mA cm−2 geometric current density, which is lower than those of IrO2, RuO2, and an ordered mesoporous Ni3N electrocatalyst.

2 Experimental

2.1 Synthesis of Mesoporous Oxides

Ordered mesoporous NiO and Ni3FeOx were synthesized following a nanocasting route with KIT-6 as the hard template according to the procedure reported by Deng et al. [26]. Typically, 0.5 g of KIT-6 and 0.8 M of metal nitrates as a precursor (Ni(NO3)2·6H2O, Fe(NO3)3·9H2O) were dispersed in 3.6 mL of ethanol in a weight ratio of 1:0 and 3:1 for NiO and Ni3FeOx oxides, respectively. After 30 min of stirring at room temperature, ethanol was removed by evaporation through heating of the mixture overnight at 60 °C. Afterward, the resulting precursor ion filled mesoporous silica
composite was heated in a ceramic crucible in an oven at 250 °C for 4 h to completely decompose the nitrate species. The impregnation step with the metal salt solution was repeated in order to achieve higher loadings. After evaporation of the solvent, the resulting metal precursor/silica composites were calcined at 550 °C for 6 h. The silica template was removed by treatment with 2 M NaOH solution, washed with deionized water and ethanol, and then dried at 60 °C for 12 h.

2.2 Synthesis of Mesoporous Ni₃N

The as-obtained mesoporous NiO (100 mg) was heated at 370 °C with a heating rate of 4 °C min⁻¹ under a flowing pure ammonia atmosphere (1 bar, 200 sccm) and maintained for 4 h in a tube furnace. The furnace was then cooled down naturally to room temperature in a flowing ammonia environment.

2.3 Synthesis of Mesoporous Ni₃FeN

The nickel–iron nitride was obtained from the mesoporous Ni₃FeOₓ mixed oxides precursor via a similar nitridation reaction: 200 mg of the porous Ni₃FeOₓ precursor was heated with a heating rate of 4 °C min⁻¹, maintained at 400 °C for 4 h under a flowing NH₃ atmosphere, and then allowed to cool to room temperature.

2.4 Zn–Air Battery (ZAB) Measurements

The Zn–air battery (ZAB) tests were performed with a homemade Zn–air cell. The air cathode was made by spraying catalyst ink onto carbon paper with a gas diffusion layer, with a catalyst loading of 0.25 mg cm⁻². The catalyst ink was prepared by ultrasonically dispersing a mixture of 6 mg Ni₃FeN, 6 mg iron phthalocyanine (FePc), 12 mL ethanol, and 100 μL of 5 wt% Nafion solution. For comparison, a mixture of 40% Pt/C and RuO₂ (mass ratio 1:1) with the same catalyst loading on carbon paper was used as the catalytic layer. A polished Zn foil (thickness 0.3 mm) was used as the anode, and the electrolyte was 6.0 M KOH containing 0.20 M Zn(Ac)₂. A Land CT2001A system was used to carry out the cycling test with a 10-min rest time between each discharge/charge cycle at a current density of 10 mA cm⁻². Each discharge/charge period was set to be 30 min. The charge and discharge polarization curves were carried out using the PINE electrochemical workstation (Pine Research Instrumentation, USA).

Further details regarding the characterization of the catalysts are available in the Supporting Information.

3 Results and Discussion

3.1 Characterization of Mesoporous Electrocatalysts

As shown in Fig. 1, highly ordered mesoporous oxides were synthesized through a nanocasting route from mesoporous silica using 3D cubic KIT-6 silica as templates [27]. In the second step, after nanocasting, the silica template is removed, leaving behind a 3D mesoporous metal oxide replica. Then, the mesoporous replica was subsequently nitridized under an ammonia atmosphere.

To verify the formation of crystalline phases, the mesoporous oxides replica and their corresponding nitrides were investigated by wide-angle X-ray diffraction (XRD). As shown in Fig. 2a, after flowing ammonia over the mesoporous NiO, the diffractogram shows completely different diffraction peaks, which are consistent with hexagonal Ni₃N (JCPDS Card No. 01-089-5144) [28]. As well for the Ni₃FeOₓ precursor, annealing at 400 °C in ammonia results in a complete conversion to an iron-nickel nitride mesostructure. The resulting XRD pattern shows only the diffraction peaks that are indexed to Ni₃FeN (JCPDS Card 50-1434). The diffraction peaks correspond to (111), (200), (220), and (311) planes of face-centered cubic (fcc) Ni₃FeN [29, 30]. None of the samples show the characteristic peak at 23° from amorphous silica (Fig. S1), confirming the complete removal of the silica template. As shown in Fig. 2b,
the low-angle diffractogram of the calcined KIT-6 shows two diffraction peaks which correspond, respectively, to the (211) and (220) reflections of a 3D Ia3d cubic structure [31, 32]. Compared with the template, all diffractograms of mesoporous oxide intermediates and their corresponding nitrides show a similar diffraction peak assigned to the (211) reflection, indicating that the ordered mesostructured is preserved. Transmission electron microscopy (TEM) analysis reveals the morphology of the pristine KIT-6 template and different as-synthesized mesoporous replicas and nitrides, as shown in Fig. 2c. The KIT-6 template consists of a highly ordered and interconnected mesopore system with a pore

![Fig. 2](image-url)

**Fig. 2**  
(a) Wide-angle XRD patterns of ordered mesoporous NiO, Ni₃N, Ni₃FeOₓ mixed oxide, and Ni₃FeN and their standard XRD JCPDS data.  
(b) Low-angle powder XRD patterns of KIT-6 and mesoporous materials replicated from KIT-6 silica. TEM images of (c) KIT-6 silica template along the [111] direction, (d) NiO, (e) Ni₃FeOₓ, (f) Ni₃N, and (g) Ni₃FeN (inset: the corresponding particles sizes distributions); (h) HRTEM of Ni₃FeN (inset: the corresponding FFT)
size diameter in the 5–6 nm range, resulting in the sharp diffraction features observed in Fig. 2b. This is also supported by the BET analysis (Fig. S2). After nanocasting, it can be observed that NiO (Fig. 2d) and Ni$_3$FeO$_3$ (Fig. 2e) exhibit an ordered framework and uniform nanoparticles with a narrow size range ~ 7 nm. Figure 2f shows the morphology of the mesoporous Ni$_3$N. We can still clearly see that the ordered mesostructure and uniform particles of the mother material, NiO, were maintained after conversion to nitride. The diameters of those particles are approximately 6.9 ± 0.4 nm (Fig. S3f), which is in good agreement with the mesopore diameter of the KIT-6 (5–10 nm). This indicates that the transformation of NiO into Ni$_3$N maintained the confined structure of the pore channels [33]. For the as-synthesized mesoporous bimetallic Ni–Fe nitride (Fig. 2g), the TEM micrograph shows that the Ni$_3$FeN partially consists of large domains with an ordered framework and uniform nanoparticles with an average size 6.3 ± 0.4 nm arranged uniformly throughout the material as expected (inset of Fig. 2g). Nitrogen sorption isotherms of Ni$_3$N and Ni$_3$FeN (Fig. S4) indicate that both of them display type IV sorption isotherm and exhibit hysteresis loops, as is typical for mesoporous materials. The template-free mesostructured nitrides have BET surface area of 50 and 52 m$^2$ g$^{-1}$ with pore size distributions ranging from 5 to 8 nm, for Ni$_3$N and Ni$_3$FeN, respectively.

Furthermore, the high-resolution TEM (HRTEM) image of Ni$_3$FeN (Fig. 2h) indicates that the fabricated mesoporous ternary nitride is well crystalized, and the integrated crystal lattice pattern suggests that a single crystal exists in this domain. The d-spacing of the plane is 1.69 Å, corresponding to the (111) plane of Ni$_3$FeN [34]. Typical selected area electron diffraction (SAED) pattern (inset of Fig. 2h) displays highly resolved concentric rings and regular spots, suggesting the high crystallinity of the sample in agreement with the HRTEM results. In addition, the energy-dispersive spectrum (EDS) elemental mapping (Fig. S7b) reveals a uniform distribution of the Ni, Fe, and N atoms in the selected field (similar to the mother oxide as shown in Fig. S6). The molar ratio of Ni/Fe in Ni$_3$FeN, determined from the EDX spectrum (Fig. S5c), is around 3.012: 0.988, close to the expected Ni/Fe ratio of 3:1.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical valence states of the various elements of the bimetallic nitride catalyst. The XPS survey spectra for Ni$_3$FeN samples (Fig. S8) confirm the presence of Ni, Fe, and N, with O and C peaks resulting from surface oxidation [35]. The Ni 2p high-resolution scans show the expected doublet Ni 2p$_{1/2}$ and Ni 2p$_{3/2}$ for various samples (Fig. 3a). As can be seen, the nitrated mesoporous materials, Ni$_3$N and Ni$_3$FeN, show a low binding energy peak centered at 852.6 eV in Ni 2p$_{3/2}$ not visible in the mother oxide template. This peak can be attributed to the metallic state of Ni [36], which results from the formation of nitride [8, 28, 37]. Additionally, there are two broad peaks centered at 855.3 and 861.2 eV in Ni 2p$_{3/2}$ with corresponding 872.7 and 879.9 eV peaks in Ni 2p$_{1/2}$. These can be described by oxidized Ni species and Ni satellite peaks, respectively [36].

Given the diffraction results, which had no significant oxide phases, this suggests that the Fe–Ni ternary nitrides samples are partially oxidized at the surface [8, 38]. The amount of metallic Ni appears to be increased with the addition of iron, as shown by the relative intensity of the metallic peak to the oxidized peaks. For Ni$_3$FeO$_3$, it is clear that the Ni oxide can be described by two components, corresponding to predominately Ni$^{2+}$ (NiO) and predominantly Ni$^{3+}$ (Ni$_2$O$_3$) oxidation states [39], while the nitrides only have one dominate oxide phase. The nitridation process seems to preferentially affect the Ni$^{2+}$ phase, which disappears with nitridation, while the Ni$^{3+}$ phase persists. This behavior is also supported by the O 1s high-resolution scans (Fig. 3d), where the O 1s of Ni$_3$FeO$_3$ has a strong feature at 529.6 eV ascribed to NiO [39], which greatly diminished with nitridation. For the mixed metal nitride, there is also evidence of an iron hydroxide phase, at 532.2 eV [40, 41]. Figure 3d shows a pure FeO$_x$ phase consisting of γ-Fe$_2$O$_3$ nanoparticles as a reference, showing a similar surface hydroxide phase [41]. Zhu et al. [38] also observed this tendency of the addition of Fe to shift the oxidation state of mixed metal oxides, which is dominated by M–OH bonds.

Figure 3b displays high-resolution Fe 2p spectra of Ni$_3$FeN, Ni$_3$FeO$_3$, as well as a reference γ-Fe$_2$O$_3$ spectra. Again, the nitridation results in the formation of a new peak at 706.9 eV, which can be assigned to metallic iron nitride [35]. However, in this case the signal is dominated by the oxide related and satellite peaks at 711.6 and 717.9 eV [35, 42]. These features are consistent with γ-Fe$_2$O$_3$, though it is difficult to unambiguously assign the oxidation states in iron oxides [41–43]. In the N 1s region (Fig. 3c), the spectrum can be deconvoluted into a combination of two components at 397.5 and 399.2 eV for nitrided samples [44].
3.2 Electrocatalytic Oxygen Evolution Reaction

An efficient oxygen evolution catalyst with superior catalytic activity requires an early-onset potential with high kinetic current density, small Tafel slope, and good durability [45]. To identify whether mesoporous iron–nickel nitride is a promising electrocatalyst for OER, electrochemical measurements were carried out by linear sweep voltammetry (LSV) on all the synthesized electrocatalysts and benchmark catalysts with the same loading density of ~ 0.203 mg cm\(^{-2}\). The upper bound of the potential was set at 1.8 V versus RHE (reversible hydrogen electrode) to avoid the detachment of the catalytic layer and interference with the measurement as a result of excessive oxygen evolution. As displayed in Fig. 4a, OER activity curves of the as-synthesized transition metal nitrides catalysts, transition metal-based oxides, and commercial RuO\(_2\) and IrO\(_2\) were all studied under the same conditions for direct comparison.

The as-prepared mesoporous bimetallic electrocatalyst iron–nickel nitride exhibited an early-onset potential of ~ 1.45 V versus RHE, high kinetic current density at a fixed potential, and the lowest overpotential (259 mV) (Fig. 4b) to achieve a current density of 10 mA cm\(^{-2}\). Compared to the nickel iron mixed oxides (352 mV), IrO\(_2\) (320 mV), RuO\(_2\) (322 mV), and NiO (415 mV), the nitrides showed the lowest overpotentials, demonstrating that the conversion of oxides to mesoporous nitrides can significantly improve the catalytic performance. Moreover, the mesoporous binary Ni\(_3\)N exhibited slightly inferior electrocatalytic activity with an overpotential of 315 mV. As predicted, after addition of Fe to form a ternary compound, the catalytic activities of metal nitrides were enhanced. The outstanding electrocatalytic performance likely originates from: (1) the synergetic effect between bimetal atoms, as reported in other bimetallic alloys such as Fe\(_{x}\)Ni\(_{1-x}\)OOH [46], Ni\(_{0.51}\)Co\(_{0.49}\)P [9], Ni–MnO/rGO aerogel [47], and NiCo\(_2\)S\(_4\) [7]; (2) hierarchical...
porosity composed of mesopores connected with macropores (or larger mesopores) facilitating fast mass transport, resulting in improved electrode performance [48–52]; or (3) a combination of these factors.

It is important to note that in the polarization curve of Ni3N, an apparent oxidation peak centered at about 1.32 V can be observed prior to the onset of oxygen evolution. This could be assigned to the oxidation redox peaks of Ni2+/Ni3+ conversion during the OER in alkaline electrolytes, which have been investigated in detail in most of Ni-based electrocatalysts [53, 54]. The shift to around 1.4 V and decrease in total Ni oxidation peak intensity in the LSV curve of Ni3FeN are likely attributed to the incorporated Fe suppressing the transformation of Ni(OH)2 to NiOOH [55], which is consistent with other bimetallic alloys (Ni,Co)S2 [56] and Fe–Ni hydroxide [55]. This suppression is also supported by the observed preferential surface oxidation of Fe in the XPS results. Additionally, it is likely that the nitridation process itself contributes to this effect, as it was mainly the Ni2+ that was converted into nickel nitride. With a limited abundance of Ni2+, there is a lower content of Ni(OH)2 in ternary nitride. These two effects likely result in a reduction in the number of active sites available for nickel oxidation. Louie et al. [57] also observed the decrease in average intensity for the oxidation state of Ni in NiOOH with the incorporation of Fe in Ni–Fe films.

The Tafel slope and current densities exchange were determined to evaluate the kinetic process. As shown in Fig. 4c, the Tafel plots derived from polarization curves demonstrate that the Ni3FeN exhibits the smallest Tafel slope of 54 mV dec−1 among these tested catalysts, which indicates efficient electron transfer and rapid kinetic activities. This is similar to the commercial heavy metal catalyst, but substantially smaller than mesoporous NiO and nickel–iron mixed
oxides (99 and 106 mV dec⁻¹, respectively). The ternary Ni₃FeN also has a lower Tafel slope than the binary Ni₃N (63 mV dec⁻¹), demonstrating more rapid kinetic activity, supporting the improved catalytic performance.

To investigate the reaction kinetics occurring at the electrode–electrolyte interface during the OER, electrochemical impedance spectroscopy (EIS) was also measured in a three-electrode system in 1.0 M KOH. On basis of the Nyquist plots (Fig. 4d), the smallest semicircle for Ni–Fe nitride suggests the lowest charge-transfer resistance for Ni–Fe nitride as evidenced by stable fixed response even after 70 h, which is superior to most of the recently reported transition metal nitrides for the OER. The superior OER activity and good stability of the as-prepared Ni₃FeN likely result from a combination of the following factors: (1) highly active electrocatalyst contact area can provide abundant accessible active sites, (2) the hierarchical porosity facilitates fast mass transport [61, 62], (3) the presence of nitrides facilitates electron/proton transfer, as well as smooth ion diffusion and transportation [63], (4) the synergistic effects of mixed metals in the ternary catalyst adjust the electronic structure and improve precipitation energies compared to single-metal materials, and (5) the favorable in situ oxidation of both metals species may play an important role in improving the catalytic activity, with the hydroxide species offering favorable active sites for hydroxyl adsorption [64]. Compared to other catalysts, particularly Co₃FeN, Ni₃FeN combines excellent OER activity, and a highly crystalline and mesoporous structure with monophase formation, with a facile synthesis method for low toxicity iron (compared to cobalt), all of which make our electrocatalyst a promising alternative for green energy hydrogen production.

### 3.3 Rechargeable Zn–Air Battery

To investigate the practical performance of mesoporous Ni₃FeN as OER electrocatalyst, a rechargeable Zn–air battery (ZAB) was made by mixing iron phthalocyanine (FePc) and Ni₃FeN with a mass ratio of 1:1 as the air cathode (Fig. 6a). The RDE measurements confirmed that FePc shows a high intrinsic ORR activity (Fig. S10), superior to commercial Pt/C in 0.1 M KOH [65, 66].

Figure 6b displays the charge polarization curves of the two air electrodes (FePc + Ni₃FeN and Pt/C + RuO₂) in ZAB, implying a better charge performance of Ni₃FeN than RuO₂ as confirmed by its higher current densities at the same potential. In addition, the charge–discharge cycling tests were carried out at current density of 10 mA cm⁻². As shown in Fig. 6c, d, Ni₃FeN + FePc exhibits a long cycle life as evidenced by stable fixed response even after 70 h, which is much longer than that (~ 20 h) of the mixed Pt/C + RuO₂
battery. More importantly, the charging voltage of Ni$_3$FeN is always lower than that of RuO$_2$, even decaying slightly over time. After the charge and discharge cycle was performed for 20 h, the charging voltage of Ni$_3$FeN is only 2.05 V, much smaller than 2.36 V of RuO$_2$. This suggests the potential application of mesoporous Ni$_3$FeN as an OER electrocatalyst superior to the conventional electrodes in a rechargeable ZAB.

4 Conclusions

This work conclusively shows the synthesis of three-dimensional (3D) ordered mesoporous Ni$_3$N and Ni$_3$FeN ternary nitrides from intermediate mesostructured metal oxide replicas with high surface areas through a hard templating method and subsequent nitridation. The products of the facile two-step synthesis process possessed a high degree of crystallinity, large specific areas, and uniform mesopore sizes (~6 nm). Ternary Ni$_3$FeN shows outstanding OER performance with very low overpotential (259 mV) to achieve a 10-mA cm$^{-2}$ geometric current density with small Tafel slope and considerable durability toward OER, which is superior to both mesoporous Ni$_3$N electrocatalysts and commercially available IrO$_2$/RuO$_2$. The enhanced catalytic performance of ordered mesoporous Ni$_3$FeN likely derives from its intrinsic activity, hierarchical porosity, abundant active sites, large contact area between the catalyst and electrolytes, synergistic tuning of electronic structure and charge...
transport characteristics, and favorable oxidation behavior. Furthermore, when combining FePc and Ni$_3$FeN as the air cathode of a rechargeable ZAB, mesoporous Ni$_3$FeN shows a much lower charge voltage and a longer charge life than RuO$_2$ in a ZAB. To summarize, these findings represent an attractive and efficient pathway toward the development of high-surface-area catalysts for electrical-chemical energy conversion. Such a platform also extends the fundamental understanding of the structure–property relationships of metal nitrides. It paves the way for the synthesis of other mesoporous ternary nitrides, which could be used in various applications, such as rechargeable ZABs and supercapacitors. Such a facile approach has the potential to provide the low-cost alternative energy sources necessary for the next-generation green technologies.

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Fig. 6  a Schematic illustration of a rechargeable Zn-air battery (ZAB) using FePc and mesoporous Ni$_3$FeN as ORR and OER electrocatalysts in the air cathode, respectively (FePc not shown here); b charge polarization curves for a battery with Ni$_3$FeN+FePc and Pt/C+RuO$_2$ as the air electrode catalysts; c, d charge/discharge cycling of a rechargeable ZAB based on Ni$_3$FeN+FePc and Pt/C+RuO$_2$ at 10 mA cm$^{-2}$. Only the charge curves were shown here to highlight the advantages of mesoporous Ni$_3$FeN used as OER electrocatalysts in a rechargeable ZAB.
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