Bio-inspired general synthesis of superplastic metal-organic framework aerogels and their applications

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Article

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Abstract

Many proposed utilizations for metal-organic frameworks (MOFs) demand their assembly into three-dimensional (3D) monolithic architectures. The capability of sustaining structural integrity during considerable deformations is important to allow a monolithic material that works reliably. Nevertheless, it remains a significant challenge to realize high superplasticity in 3D macroscopic MOF networks. Here we report the ice-template-driven assembly of MOF nanobelts to form superelastic MOF-based cellular aerogels. Inspired by the hierarchical architecture of natural cork, the resulting materials can fully and rapidly recover its initial architecture after 50% strain compression and unloading for 2000 cycles. The characteristic hierarchical structure can be extended to single (Ni-, Mn-, and Co-), binary (NiMn-, NiCo-, and CoMn-), and ternary (NiCoMn-) MOF aerogels with exceptionally structural and chemical properties. Potential application has been further demonstrated for NiMn-MOF aerogels in flexible energy conversion, which can effectively electrocatalyze hydrogen evolution in natural seawater even in the presence of considerable electrode deformations. The successful fabrication of such a class of fascinating architectures opens up enormous opportunities for exploring new application of MOFs in a free-standing, structurally adaptive, and macroscopic form.

Introduction

Metal-organic frameworks (MOFs) represent a class of materials with the combination of extraordinary porous, structural, and chemical properties, which would become a new emerging nanoscale building block for constructing macroscopic assemblies for a broad range of applications. Some techniques, such as self-gelation, have recently been developed to fabricate highly porous MOF aerogels. However, similar to most of the existing porous materials, the resulting MOF aerogels are brittle and have small recoverable deformation before failure. Superelasticity that has been observed in 3D architectures made of many other materials has not been achieved in MOFs. Indeed, MOFs are especially fragile, in the common view, and they are far from the stage of superelasticity development. Previous analysis suggests that it would be significantly challenging to realize superelasticity in three-dimensional (3D) MOF assemblies. The capability of sustaining structural integrity during considerable deformations for 3D MOF assemblies is not only crucial for fabricating new categories of flexible energy devices, such as electrocatalysis, batteries, and supercapacitors, but also critical for future design of macroscopic MOF-based biological tissues resistant for mechanical damping. It is therefore highly desirable to explore new strategies to address this challenging yet very important problem.

Generally, the macroscopic behaviors of materials are dominated by their intrinsic microscopic properties, for example, the underlying geometries. In nature, corks have been recognized as one of the oldest materials exploited by human beings. The state-of-the-art structural analyses have been conducted to examine the microstructures of corks that feature exceptional mechanical robust. In a cork structure, one-dimensional (1D) nanofibers of cell walls are intimately arranged in a highly oriented manner to reach the reasonable strength. Further, individual cells of tens of micrometres in size are then closely
connected to produce a 3D honeycomb-like architecture, which has proven to be very useful to maximize bulk superplastic modulus. Therefore, we surmise that efficient and ordered assembly at hierarchical structural levels is critical for cork to realize high mechanical elasticity.

Inspired by the striking hierarchical architecture of nature cork, we consider that MOF monoliths might deliver excellent mechanical properties if assembly in a reasonable manner similarly to cork. Consequently, based on our most recent research on the controllable manipulation of low-dimensional MOF materials,\textsuperscript{16} here we report a general procedure for building MOF architectures, starting by a one-step hydrothermal method to synthesize 1D MOF nanobelts followed by the ice-template-driven assembly of MOF nanobelt into a 3D hierarchical aerogels. The as-resulted NiMn-MOF nanobelt aerogel exhibits superelasticity, in addition to many other excellent structural properties such as highly exposed active centers, hierarchical pore structure, and good electrical conductivity. We further demonstrate the NiMn-MOF aerogels as a new class of flexible electrodes for hydrogen evolution reaction (HER) in natural seawater.

**Results**

**Synthesis and formation process of superplastic MOF aerogels.** As a proof-to-concept experiment, we describe the preparation of NiMn-MOF aerogel by a two-step procedure (Fig. 1). In the first step of producing 1D NiMn-MOF nanobelts, nickel and manganese acetate salts were mixed with organic ligand of 2-thenoic acid in an ethanol solution, which was subjected to hydrothermal treatment at 150 °C. By tuning different hydrothermal durations, we examined the reaction intermediates. We found irregular nano-particles without apparent elemental segregation for the NiMn-MOF precursor before 30 min by scanning electronmicroscopy (SEM) and SEM elemental maps, indicating that the metal ions and ligands began to nucleate within this period (Fig. 1d, Supplementary Figs. 1a,b and 2a-d). During the hydrothermal reaction from 1-4 hrs, we have observed a mixture of irregular nano-particles and nanobelts, indicating that crystal growth process has occurred (Fig. 1d, Supplementary Figs. 1i-n and 2e-l). Further, the crystals have continuously grown at 6-8 hrs by showing the increased length of nanobelts, which completed at 10 hrs by showing little shape change (Fig. 1d, Supplementary Figs. 1e-l and 2m-p).

According to the literature\textsuperscript{17,18} and XRD patterns (Fig. 2i and Supplementary Fig. 16), the as-formed NiMn-MOF is consisted of alternating organic units (2-thenoic acid group) and inorganic units (Ni or MnO\textsubscript{6}), where the carboxyl group of each ligand bridges two metal atoms, and each metal ion coordinates to two opposite carboxyl groups and four equatorial ethanol molecules (Fig. 1). Other MOF nanobelts, including Ni-MOF, Mn-MOF, Co-MOF, NiCo-MOF, CoMn-MOF, NiCoMn-MOF, were synthesized by a similar method except of using different metal sources (Supplementary Figs. 17, 19).

In the second step of hierarchical assembly of 1D MOF nanobelts into 3D aerogels, NiMn-MOF was dispersed in aqueous solutions with different mass concentrations, and subjected to freeze-dry treatment (Inset of Fig. 2a). Both FT-IR (Fig. 2l, Supplementary Fig. 18) and Zeta potential analyses (Supplementary Fig. 4) verify the presence of a large number of hydroxyl and carboxyl functional groups on the surface of
NiMn-MOF, which promote their good dispersibility in water (Supplementary Fig. 5). The MOF nanobelts in aqueous solution was then freezed in liquid nitrogen, where they are forced to align along the direction of ice solidification movement (Figure 1a),\textsuperscript{19,20} resulting in a highly ordered and anisotropic 3D structure. During this process, the as-produced microstructures are affected by a number of factors, such as dispersion concentrations, dry method and freezing speed.

Consequently, we adjust the dispersion concentrations of NiMn-MOF nanobelts from 0.2 to 8.3 mg cm\textsuperscript{-3}). The aerogel architecture obtained at a low concentration (< 1.3 mg mL\textsuperscript{-1}) is randomly oriented nanobelt cross-linked fluffy network structure, and did not shows any superplastic property during compression-unloading test (Fig. 1a). When the concentration of NiMn-MOF reaches 3.6 mg mL\textsuperscript{-1} and above (such as 5.9 mg mL\textsuperscript{-1}), these 1D nanobelts can assemble into ordered 2D array, and further to honeycomb network-like superplastic 3D aerogel (Figs. 1b, c). In addition, the dry method is also important to the formation of 3D NiMn-MOF aerogel, as we can only obtain powder-like samples by drying at 60 °C in air (Supplementary Fig. 6). Further, even for the freeze-drying method, the freeze speed should also be manipulated with care. The rapid freezing by liquid nitrogen (freezing rate: 50 °C min\textsuperscript{-1}) can only generate disordered cross-linked aerogels (Supplementary Figs. 7c,d) with poor mechanical property (Supplementary Figs. 7a,b). As a consequence, we tune the freezing speed slowly from bottom to top (5 °C min\textsuperscript{-1}), which introduce water condensation in vertical direction, and force 1D NiMn-MOF nanobelts to assemble into 2D sheet arrays along the leading edge of ice movement. Finally, these 2D nanosheets are laterally connected into a highly ordered 3D compressible MOF aerogel after thawing (Figs. 1, 2a~c). The general procedure has been extended to fabricate other 3D superplastic MOF aerogels composed of single (Ni-, Co-, Mn-), binary (NiCo-, CoMn-) and ternary (NiCoMn-) metal elements (Supplementary Figs. 8-13).

**Morphology and structure characterizations of superplastic NiMn-MOF aerogel.** The optical image shows NiMn-MOF that is present as a solid yellow-gray cylinders of a few centimeters size with a small mass density of 3.6 mg cm\textsuperscript{-3} (inset of Fig. 2a), which is similar to previously reported MOF aerogels.\textsuperscript{4} The macroscopic aerogel is made of ordered 2D sheet array with the adjacent sheet spacing of approximately 15 μm (Figs. 2a,b), which are further composed of flexible 1D nanobelts of 400 nm width, 1.37 nm thickness, and tens of micrometers lengths (Figs. 2c-f). The high-resolution TEM (HRTEM) image shows good crystallinity of NiMn-MOF with lattice fringe spacing of 0.25 nm (Fig. 2e). Further, TEM element mapping shows the homogeneously distribution of Ni, Mn, S, O and C elements throughout nanobelts (Fig. 2f).

The structure of NiMn-MOF was characterized X-ray photoemission spectroscopy (XPS) that indicate the atomic ratio of 61.1% for Mn/Ni, which is consistent with the result of energy dispersive X-Ray spectroscopy on SEM (Supplementary Figs. 14,15a). In Fig. 2g, XPS Ni 2p profile has been deconvoluted into Ni 2p\textsubscript{3/2} at 855.9 eV, Ni 2p\textsubscript{1/2} at 873.5 eV and their satellites at 861.5 (Ni 2p\textsubscript{3/2}) and 879.6 eV (Ni 2p\textsubscript{1/2}). Therefore, the oxidation state of the Ni species is determined to be +2 (Fig. 2g). Similarly, XPS Mn 2p profile exhibits Mn 2p\textsubscript{3/2} at 641.7 eV, Mn 2p\textsubscript{1/2} at 653.3 eV, and satellites at 645.8 eV, which identify +2
oxidation state for Mn inside NiMn-MOF (Fig. 2h).\textsuperscript{21} Further, we analyzed the XPS S 2p\textsubscript{3/2} at 164.1 eV and S 2p\textsubscript{1/2} at 165.3 eV that indicate the C-S-C chemical bond in the organic ligand (Supplementary Fig. 15b);\textsuperscript{22} and the peaks of the O1s at 530.4, 531.3 and 532 eV attributed to O-M (Ni, Mn), C=O and -OH from metal nodes of MOF materials (Supplementary Fig. 15c).\textsuperscript{23} These results are consistent to other structural characterizations including X-ray diffraction (Fig. 2i, Supplementary Fig. 16) and FT-IR (Fig. 2l, Supplementary Fig. 18).

Commonly, MOFs are considered as poor electrical conductors (usually 10\textsuperscript{-10} S m\textsuperscript{-1}) that limit their applications in the field of electrical devices and electrochemistry.\textsuperscript{24,25} Therefore, the electrical conductivities of MOFs have been measured. The NiMn-MOF shows the highest conductivity of 2.09±0.64 S m\textsuperscript{-1} as comparison to other samples including Ni-MOF (0.23±0.05 S m\textsuperscript{-1}), NiMn-MOF (25% of Mn, 0.73±0.21 S m\textsuperscript{-1}), NiMn-MOF (80% of Mn, 1.60±0.23 S m\textsuperscript{-1}), and Mn-MOF (0.63±0.23 S m\textsuperscript{-1}, Fig. 2k, Supplementary Table 1). This result is consistent to the theoretical simulations of electron location function (ELF) and the density of states (DOS) by density function theory (DFT, Fig. 2j and Supplementary Figs. 20). As shown in Fig. 2j, the correlation ELF value between the metal node and the adjacent organic ligand in the NiMn-MOF is between 0.4 and 0.5,\textsuperscript{26} indicating that the MOF is metallic in character. Also, the density of states (DOS) of Ni, Mn and overall atoms across the Fermi level in the computed density of state (DOS) for the NiMn-MOF, which indicates the material an intrinsic conductivity (Supplementary Figs. 20). The above results unambiguously confirm that a superplastic NiMn-MOF aerogel with excellent electrical conductivity has been successfully fabricated, which can be used as a potential catalyst for electrolytic hydrogen evolution from seawater.

**Superplastic properties and applications of MOF aerogels.** To characterize the superplasticity of our MOFs, three MOF examples composed of Co- (single counterpart), NiMn- (binary counterpart) and NiCoMn- (ternary counterpart) metal sites were selected for mechanical property studies. The optical images in Figs. 3a,d,g illustrate a compression-resilience cycle test for Co-MOF, NiMn-MOF and NiCoMn-MOF starting by applying 50% strain of initial state. Interestingly, these MOFs aerogel can restore its original shape once the applied force was unloaded, and finally to the fully extended initial state within 1 s. The compression-resilience cycle was repeated for 2,000 times, and their shape degradations are almost negligible, i.e., 8.3% for Co-MOF, 2.9% for NiMn-MOF, and 3.8% for NiCoMn-MOF (Figs. 3c,f,i).

Moreover, the microstructures of Co-, NiMn-, and NiCoMn-MOFs during compression-resilience cycle test were examined by SEM images. Figs. 3b,e,h clearly displays the anisotropic layered structure of Co-MOF, NiMn-MOF and NiCoMn-MOF aerogels, where the adjacent layer spacing change from 22 to 6 μm, 95 to 20 μm and 25 to 6 μm after applying 50% strain to the MOF architecture, respectively. The layer spacing restore to 21 μm for Co-MOF, 90 μm for NiMn-MOF and 23 μm for NiCoMn-MOF after the external force release within 1 s. The above phenomenon is similar to many other superplastic materials like graphene and polymers,\textsuperscript{8,27} indicating excellent superplasticity of our MOF aerogels.
Next, we demonstrated the potential applications of our superplastic MOF aerogels as a new class of flexible electrodes for hydrogen evolution reaction (HER) in seawater. As we know, flexible energy systems have attracted considerable interest because of their remarkable properties such as small-size unit, lightweight, and shape conformability, which are promising components for versatile portable, foldable, and wearable devices.\textsuperscript{16,28-30} However, the currently reported hydrogen evolution systems are generally fabricated in the form of bulky and heavy architectures, indicating that they are far behind the requirement of flexibility. Conventional electrodes are synthesized by depositing of powder or thin-film form electrocatalysts, such as MOFs and others,\textsuperscript{31-33} onto rigid substrates (like glassy carbon\textsuperscript{31,32} and FTO glass\textsuperscript{33}), only resulting in bulk and fragile electrolytic devices. Very recently, several soft current collectors (such as carbon-fiber paper\textsuperscript{30} and metal foams\textsuperscript{16,28}) have been employed to make HER catalyst electrodes by taking advantages of their excellent properties of high electrical conductivity, interconnected porous networks, and mechanical robust. Integrating these soft substrates with catalytic active species has been achieved by the synthetic strategies of solution-casting or direct growth. However, owning to the intrinsically fragile nature of powders or thin-films, the flexible behaviors of as-resultant electrodes are still compromised, leading to considerable activity decay in the process of electrode deformations.

Here we firstly demonstrated the electrochemical hydrogen evolution by using a superplastic MOF aerogels with favorable activity, flexibility, kinetics, and stability. Technically, NiMn-MOF was interwoven with nickel foam to produce a catalytic electrode. The as-resultant electrode can promote hydrogen evolution from both simulated seawater (NaCl, Supplementary Figs. 21-26, Tables 4-7) and natural seawater (collected from the Yellow Sea in Qingdao, China). Owning to the flexible properties of both NiMn-MOF and nickel foam, the electrodes can work both without and with folding deformations. Without deformations, the linear scanning voltammetries (LSVs) curves of NiMn-MOF electrode show a small overpotential of \(\sim 243\) mV at the current density of 10 mA cm\(^{-2}\), comparable to that obtained from simulate seawater (3 wt% NaCl, Supplementary Fig. 21). Even under the high current density of 200 mA cm\(^{-2}\), the HER overpotential of NiMn-MOF is only \(\sim 341\) mV. To our best knowledge, our NiMn-MOF is the most active electrocatalysts reported in the literature (Supplementary Table 7).

Notably, the activities of catalyst electrodes show little change after structural deformations. The overpotentials after one-, two-, and three-foldings have slightly increased to 270, 264 and 258 mV at the current density of 10 mA cm\(^{-2}\), which are 354, 343, and 361 mV at 50 mA cm\(^{-2}\), and 362, 362, and 386 at 100 mA cm\(^{-2}\) (Figs. 4a,b, Supplementary Table 6). Even under the high current density of 200 mA cm\(^{-2}\), the HER overpotential only increases to 364, 372, and 394 mV after significant deformations of one-, two-, and three- folds (Figs. 4a,b, Supplementary Table 6). To our best knowledge, such mechanically robust electrodes with excellent activities have never been reported before.

Importantly, the catalyst electrodes also show excellent reaction kinetics after deformations, as verified by the similar Tafel slopes and charge-transfer resistance (\(R_{ct}\)) from EIS analysis in Fig. 4c and Supplementary Table 6. The Tafel slopes only declines slightly from 126 (no folded) to 139 (1\textsuperscript{st} folded),
121 (2\textsuperscript{nd} folded) and 163 mV dec\textsuperscript{-1} (3\textsuperscript{rd} folded). Similarly, the electrochemical impedance spectroscopy (EIS) measurements of NiMn-MOF electrodes did not change with folding, which shows a charge-transfer resistance ($R_{ct}$) of 2.2 Ω for no folds as comparison to 2.1 Ω for 1\textsuperscript{st} folds, 1.4 Ω for 2\textsuperscript{nd} folds, and 1.9 Ω for 3\textsuperscript{rd} folds (Fig. 4d and Supplementary Table 6).

Remarkably, all the electrodes with different folds exhibit excellent electrochemical durability, as revealed by the chronopotentiometry with negligible overpotential increase for 12 hrs (Fig. 4e) and identical LSV and EIS before and after testing (Fig. 4f). This excellent electrochemical durability is further confirmed by the SEM, elemental mappings, XRD and FT-IR before and after testing (Supplementary Figs. 27-29). All the above results show that the NiMn-MOF electrode has high physical flexibility, stability and mechanical integrity, and can be used as a flexible catalytic electrode for natural seawater splitting.

To gain mechanism insights into the HER at NiMn-MOF catalyst, we have conducted a series of density functional theory (DFT) calculations to investigate the catalytic reactions by calculating the Gibbs free energy of H* adsorption, which has been considered as a key descriptor to characterize the HER activity of the electrocatalysts.\textsuperscript{34-37} Firstly, the Gibbs free energy of H* adsorption on NiMn-MOF surface was calculated at different active sites (Ni, Mn, and O sites) with the most energy stable configurations shown in Fig. 4h and supplementary Fig. 30. Generally, an electrocatalyst with a positive value represents low kinetics of hydrogen adsorption, while a negative value means low kinetics of hydrogen desorption. The optimum value of $|\Delta G|$ should be zero. For NiMn-MOF, the $\Delta G_{H^*}$ of Mn and O active sites is quite positive (0.991 eV) or negative (-1.51 eV), which indicates a strong interaction between H* and these active sites, manifesting in poor HER reaction kinetics. While at the Ni active sites, $\Delta G_{H^*}$ shows the optimal value of -0.709 eV, demonstrated significantly improved activity for HER (Fig. 4h). Therefore, Ni should be the main active sites for HER proceeding on NiMn-MOF surfaces. Further, the $\Delta G_{H^*}$ of NiMn-MOF is compared with those of bare Ni-MOF and Mn-MOF surfaces calculated by a similar method (Fig. 4i, Supplementary Fig. 31). NiMn-MOF shows a much smaller Gibbs energy of -0.709 eV than bare Ni-MOF (1.10 eV) and Mn-MOF (2.65 eV), thus indicating the strong synergistic effect between Ni and Mn atoms inside the hybrid MOF architecture (Fig. 4i). This result is also consistent to the configuration change inside NiMn-MOF with the Ni-H bonding length reduced by 0.01 angstrom as comparison to bare Ni-MOF without Mn doping.

The significantly enhanced HER performances of superplastic NiMn-MOF aerogel is originated from its excellent structural properties. Firstly, the large surface area of NiMn-MOF has been examined by N\textsubscript{2} isotherms, which shows the Brunauer-Emmett-Teller (BET) specific surface area 2.6 times larger as comparison to its powder counterpart (11.8 vs. 4.6 m\textsuperscript{2} \text{g}\textsuperscript{-1}, Supplementary Fig. 32, Table 3).\textsuperscript{38} This result is consistent to electrochemical double-layer capacitance ($C_{dl}$) test in Supplementary Figs. 33,34 and Table 4, where the $C_{dl}$ of NiMn-MOF is 11.25 mF cm\textsuperscript{-2} and roughly 3 times larger than that of powder counterpart (3.92 mF cm\textsuperscript{-2}). In addition, the competition co-ordination between metals (Ni or Mn) with different electronegativity and oxygen (O) forms an asymmetric M-O covalent bonds, which determine the exposure of cationic active sites. This result is consistent to Zeta potential, XRD and FT-IR change in Figs.
2i,l and 4g, which proves that the bimetallic synergy can produce higher exposure metal active sites. Secondly, we find the NiMn-MOF with excellent electrical conductivity, which is different from traditional MOF materials. The electrical conductivity have been examined by experiments, as well as ELF and DOS theoretically (Figs. 2j,k, Supplementary Fig. 20, Table 1), which can be explained by the strong coordination between metal ions and organic ligands. The conductive MOF nature can ensure fast charge transport within electrodes that afford excellent catalytic activity.

Thirdly, from the perspective of microstructure, NiMn-MOF aerogel is a multi-level porous structure made of 1D nanobelts assembled into 3D macroscopic architecture. During applying strains, the mutual repulsion between organic groups (-OH and -COOH from 2-thenoic acid) on the surface of the nanobelts can reduce the effect of external forces which is easy to recover after loading release. As a consequence, the NiMn-MOF electrode has worked stably even after three-folding deformation. The hierarchically porous structure of NiMn-MOF can also provide enormous voids between adjacent nanobelts that can buffer the strains/stress during vigorous gas evolution within electrodes, thereby allow for excellent durability in catalytic reactions.

**Conclusion**

In conclusion, this work has reported that superelastic MOF-based 3D monoliths could be fabricated by mimicking the hierarchical architecture of nature cork via a low-cost, solution-based procedure. Characteristic of the attractive properties of superelasticity with a good recovery rate, excellent electrical conductivity, high activity and stability of hydrogen evolution from seawater electrolysis all combined together, we expect that such exceptional functional materials will pave the way for a broad range of technological applications. Particularly, our work would allow for exploring the properties and utilizations of MOFs in a self-supporting, structurally flexible, and 3D macroscopic form. Furthermore, a wide range of functional materials may be readily introduced into the open micro-, meso-, and macropores inside MOF aerogels, offering plenty of space to develop many new MOF-based hybrid nanomaterials for applications such as photocatalysis, carbon dioxide electroreduction, metal-air batteries, biosensors, and adsorption.

**Declarations**

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**Author contributions**

Y.S. and S.X. contributed equally in this work. S.C. and J.Z. designed the research; Y.S. and S.X. synthesized the samples and performed the characterizations; S.C., J.Z., and X. W. discussed and all authors co-wrote the manuscript.
Additional information

Supplementary information accompanies this paper at www.nature.com/naturecomminications. Correspondence and requests for materials should be addressed to J.Z. or S.C.

References


**Figures**
Figure 1

Schematic synthesis of superplastic nickel, manganese (NiMn)-metal-organic framework aerogels. (a) SEM images and schematic of NiMn-MOF with the concentration of (a) 0.87 mg mL$^{-1}$, (b) 3.6 mg mL$^{-1}$ and (c) 5.9 mg mL$^{-1}$ (scale bars for a, b, c are 30 μm, 30 μm and 20 μm); (d) SEM image of reaction intermediates for superplastic NiMn-MOF aerogels at different reaction durations (scale bar: 1 μm).
Figure 2

Morphological and structural characterizations of nickel, manganese-metal-organic framework aerogels. (a~c) SEM images (scale bars for a, b, c are 100 μm, 20 μm and 200 nm); inset of (a) is an optical image; (d) TEM image (scale bar: 10 nm); (e) HR-TEM image (scale bar: 5 nm); (f) TEM element mapping of Ni, Mn, S, O and C (scale bar: 200 nm); (g, h) XPS Ni 2p and Mn 2p spectra; (i) XRD patterns in comparison to those of Ni-MOF and Mn-MOF; (j) Electron location function; (k) Electrical conductivity of NiMn-MOF.
synthesized from different manganese feeding percentages; (l) FT-IR spectra as comparison to that of organic ligand of 2-thenoic acid.

Figure 3

Mechanical properties of different metal-organic framework aerogels. (a-c) Co-MOF aerogels; (d-f) NiMn-MOF aerogels; (g-i) NiCoMn-MOF aerogels; (a,d,g) Optical image for elasticity test; (b,e,h) SEM images for elasticity test (scale bars: 10 μm); (c,f,i) Compression-unloading performances.
Figure 4

Electrocatalytic performances and mechanism studies of nickel, manganese-metal-organic framework aerogels for hydrogen evolution in natural seawater. The flexible catalyst electrode was prepared by intervolving MOF aerogels with nickel foam substrate, which was achieved by introducing nickel foam in the synthetic step of MOF aerogels. (a) LSV curves of NiMn-MOF with different folding times of electrodes; (b) the corresponding overpotentials at different current densities; (c) the corresponding Tafel plots; (d) the corresponding EIS plots; (e) the corresponding stability test for 12 hrs; the inset of panel (e) shows corresponding optical images for flexible catalyst electrodes with different folding times; (f) LSV curves of NiMn-MOF before and after stability test, inset of (f) are EIS plots; (g) mechanism study by zeta potentials in relation to the feeding ratios (w/w) of metal salts (Ni and Mn) inside NiMn-MOF; (h) Gibbs energy diagrams of NiMn-MOF for HER at different active sites; (i) Gibbs energy diagrams of NiMn-MOF, Ni-MOF, and Mn-MOF for HER.
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