Precise anionic regulation of NiFe hydroxysulfide assisted by electrochemical reactions for efficient electrocatalysis†

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Highly efficient electrocatalysts with high intrinsic activity for oxygen and sulfur redox reactions are strongly required for sustainable energy systems. Generally, cations serve as the real active sites in transition metal compound electrocatalysts, whose electrocatalytic activity is regulated by the surrounding anionic structure. Herein, an electrochemical reaction assisted by an anionic regulation strategy is proposed for precise construction of advanced electrocatalysts with extraordinary electrocatalytic activity. The electrochemical anionic regulation process ensures general release of the regulation reagents for precise substitution of sulfur anions in pristine hydroxide. The as-obtained hydroxysulfide electrocatalyst exhibits a desired electronic structure to afford superb electrocatalytic activity regarding reduced overpotential of 286 mV at 10 mA cm⁻² for electrocatalytic oxygen evolution and improved polysulfide redox electrocatalytic activity. This contribution not only renders an emerging strategy for precise regulation of the anionic structure for improved electrocatalytic activity, but also provides information for the rational design of advanced electrocatalysts for sustainable energy applications.

Introduction

Investigations into clean and renewable energy systems, such as water splitting,¹⁻³ metal–air batteries,⁴,⁵ and lithium–sulfur (Li–S) batteries,⁶,⁷ are strongly considered as a vital means to address current global challenges. These next-generation energy storage devices usually rely on multi-electron conversion reactions based on a series of oxygen/sulfur-containing substrates at the cathode, involving oxygen evolution reactions (OERs)⁸,⁹ and polysulfide redox reactions.¹⁰ However, the kinetics of these redox reactions are very sluggish, rendering large charge/discharge voltage gaps, reduced energy efficiency, and poor cycling life.¹¹⁻¹⁴ Consequently, kinetically unfavorable cathode reactions severely limit the performances of the abovementioned energy storage devices.

Advanced electrocatalysts to accelerate the cathode redox reactions are required.¹⁵,¹⁶ Transition metal compounds are highly regarded as ideal electrocatalysts due to their abundance, facile fabrication, and high electrocatalytic activity.¹⁷,¹⁸ In the transition metal compounds, cations are generally regarded as the active sites to interact with the oxygen/sulfur-containing feedstocks.¹⁹ The electronic structure of the cations is therefore essential for superb electrocatalytic performance.²⁰⁻²² Anions, on the other hand, serve as electronic donors and regulate the electronic structure of the adjacent cationic active sites through ionic polarization.²³ Therefore, an optimum anionic structure is also significant to achieve excellent electrocatalytic activity on transition metal compound electrocatalysts.

Broader context

Growing energy demand and severe environmental pollution mean that clean and renewable energy systems, such as metal–air batteries and lithium–sulfur batteries, are required. However, the performance of these energy systems are strongly limited by the kinetically unfavorable oxygen/sulfur-based conversion reactions in the cathode. Therefore, high-performance electrocatalysts with intrinsic activities for oxygen/sulfur-based redox are urgently required. In transition metal compound electrocatalysts, cations are regarded as the active sites, whose electrocatalytic reactivity can be regulated by the anionic structure. Anionic regulation is therefore proposed as an efficient strategy for the rational construction of the anionic structure to modulate electrocatalytic performances. Unfortunately, precise anionic regulation to construct desired hetero-anionic structures still remains challenging. In this contribution, an electrochemical assisted anionic regulation strategy was proposed for precise construction of the hetero-anionic structure to obtain high-performance electrocatalysts. This work affords an efficient strategy for the precise anionic regulation and provides instructions for the rational design of high-performance electrocatalysts for next-generation energy devices.
Anionic regulation has been proven to be an efficient strategy for rational construction of the anionic structure surrounding the cation active sites.\textsuperscript{23,24} During anionic regulation, a portion of pristine anions are substituted with extraneous anions to afford a multi-anionic compound.\textsuperscript{25} The as-obtained multi-anionic compound exhibits a hetero-anionic structure with atomically distributed polarized and non-polarized anions. Through anionic regulation, the polarization degree of the cation active sites can be sufficiently modulated by the hetero-atomic structure, leading to a favorable electronic structure for efficient electrocatalysis.\textsuperscript{26} For instance, a ZnFe oxy sulfide electrocatalyst was obtained by doping Se\textsuperscript{2−} into ZnFe hydroxides to regulate the electronic properties for OER promotion by Lee and co-workers.\textsuperscript{27} Similarly, hydroxysulfide,\textsuperscript{19,28} oxynitride,\textsuperscript{29} phosphosulfide,\textsuperscript{30} oxyphosphorhide,\textsuperscript{24,31} nitrophosphide,\textsuperscript{32} and sulfiselenide\textsuperscript{33} with hetero-atomic structures were fabricated as advanced electrocatalysts. Meanwhile, the anionic regulation strategy expands the variety of the electrocatalysts from single-anionic compounds to multi-anionic compounds to provide extended candidates. Therefore, the anionic regulation strategy has been highly regarded as a general approach to achieve high-performance electrocatalysts.\textsuperscript{34}

Despite the above advantages, precise construction of the hetero-anionic structure remains a tough issue. Different anions from transition metal cations, most anions are distinguishable from each other in ionic charge and radius. For instance, same-period nitrogen, oxygen, and fluorine anions are different in ionic charge, while same-group oxygen, sulfur, and selenium anions exhibit ionic radius of 140, 184, and 198 pm, respectively. Therefore, the integration of different anions to construct the hetero-anionic structure is intrinsically challenging. The current implementation of anionic regulation by random extraneous anion substitution usually results in anion aggregation and phase collapse rather than providing the hetero-anionic structure. For instance, after directly treating NiFe hydroxide with sulfur-containing reagents, undesired new phases corresponding to FeNi\textsubscript{xs} and FeNi\textsubscript{xs} were identified.\textsuperscript{19} Besides, undesired metallic phosphide, nitride, and selenide were also obtained during the anionic regulation process with phosphorus,\textsuperscript{24} nitrogen,\textsuperscript{29} and selenium anions,\textsuperscript{27} respectively, due to the unavoidable aggregation of extraneous anions. Therefore, direct anionic substitution through uncontrolled chemical anionic exchange is not able to precisely construct the desired hetero-anionic structure. If the anionic regulation process is precisely controlled with accurate anionic substitution, the as-obtained electrocatalyst with precisely-modulated hetero-anionic structure, can demonstrate superior electrocatalytic performances in clean and renewable energy storage processes.

In this contribution, an electrochemical reaction assisted anionic regulation strategy was proposed for the precise construction of the desired hetero-anionic structure to obtain highly-active electrocatalysts for OER and polysulfide redox reactions (Fig. 1). The electrochemical reactions are highly controllable by monitoring the electrical signals, compared with uncontrolled chemical anionic exchange in solution. Further, the rate and extent of the electrochemical reactions can be monitored via the applied current and voltage for controllable generation of the extrinsic anions. Herein, successful anionic regulation was realized to afford a novel hydroxysulfide with oxygen–sulfur hetero-anionic structure endowed by electrochemical release of polysulfide on the hydroxide precursor. Consequently, the precise anionic-regulated hydroxysulfide electrocatalyst demonstrates a favorable electronic structure for the cationic active sites with superb OER performance (286 mV at 10 mA cm\textsuperscript{−2}) and prominent kinetic promotion for the polysulfide redox reactions.

**Results and discussion**

To verify the feasibility of the electrochemical assisted approach for precise anionic regulation, a sulfur electrode was fabricated for controllable release of polysulfides that interacted with the NiFe layered double hydroxide (LDH) to afford the anionic regulated NiFe hydroxysulfide electrocatalyst. NiFeLDH was hybridized with a conductive graphene framework (GF; Fig. S1, ESI\textsuperscript{†}) as the precursor (named as LDH-0), where the GF served as the conductive scaffold to load the electrocatalyst, and a porous template to render the NiFeLDH with nanosized morphologies (Fig. S2, ESI\textsuperscript{†}).\textsuperscript{35} X-ray diffraction (XRD) patterns of LDH-0 (Fig. S3, ESI\textsuperscript{†}) confirm the hydroxide phase of NiFeLDH (PDF\# 38-0715). Additionally, both X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) indicate the atomic Ni/Fe ratio is close to the theoretical value of 3.0 (Fig. S4, ESI\textsuperscript{†}). The definite constitution and nanosized morphology guarantee LDH-0 to be an ideal precursor for further anionic regulation.

The electrochemical reaction assisted anionic regulation was performed on NiFeLDH with polysulfides as the extrinsic anions for substitution. The generation of polysulfides was realized in a Li–S cell. The Li–S cells were cycled at the voltage range of 2.11–2.35 V to reversibly generate soluble polysulfides and avoid the formation of solid Li\textsubscript{2}S/Li\textsubscript{2}S\textsubscript{3} and intercalation of lithium ions in LDH as interferents.\textsuperscript{36,37} Additionally, to control the anionic regulation degree of the NiFeLDH precursor, each sample was treated with different cycle numbers in working Li–S cells. Fig. 2a reveals the voltage–time curve of the Li–S cell used for the electrochemical assisted anionic regulation. The as-obtained samples were named as LDH-x, where x refers to the cycle number. LDH-0, LDH-1, LDH-5, and LDH-10 were
The efficiency of the electrochemical assisted anionic regulation was first evaluated by morphology and structural characterization. The LDH-x electrocatalysts share similar morphologies to nanoplates around 5 nm in size hybridized with GF (Fig. 2b–e and Fig. S2, S5–S7, ESI†). The nanoplates are well maintained without obvious agglomeration or detachment. The analogous morphologies suggest no aggregation of the extrinsic sulfur anions that would destroy the hydroxide phase and afford an additional sulfide phase. Further XRD patterns validate the preservation of the main hydroxide phase in agreement with the morphology characterization (Fig. 3a). No nickel or iron sulfide can be identified, indicating the introduced sulfur anions are atomically dispersed without aggregation. The maintained morphology and bulk structure afford advantageous evidence for the precise construction of the hetero-anionic structure.

The composition of the anionic regulated samples was analysed by XPS and EDS to evaluate the substitution of hydroxyl anions with sulfur anions during the electrochemical anionic regulation process (Fig. S4, S8–S10 and Table S1, ESI†). Both XPS and EDS results exhibit a stable atomic ratio of Ni/Fe as the NiFeLDH precursor (Fig. 3b). The stable Ni/Fe atomic ratio indicates the maintained bulk structure without digestion of the metallic cations. On the other hand, with increased cycle numbers, the atomic ratio of S/M (M refers to the transition metal elements) primitively rises and gradually stabilizes to 0.7 for XPS and 0.4 for EDS (Fig. 3c). The correlation of the S/M ratio with the cycle number indicates that sulfur anions gradually substitute the original hydroxyl anions in the hydroxide precursor. It is worth mentioning that, the S/M ratio detected by XPS is higher than that by EDS, which indicates that the substitution of sulfur anions mainly occurs on the surface of the electrocatalysts, considering that XPS has a shallower detection depth than EDS. That is, only the electrocatalyst surface was transformed into amorphous hydroxysulfides, while the inner part still remained as hydroxides, which is thereby fabricated, respectively. With the increase of the cycle number, the charge/discharge capacity capacity reduced accordingly, partly due to the consumption of polysulfide during the anionic regulation process.

Fig. 2 Electrochemical anionic regulation process. (a) Galvanostatic discharge/charge curves of the Li–S cell reactor. TEM images of (b) LDH-0, (c) LDH-1, (d) LDH-5, (e) LDH-10.

Fig. 3 Material characterization of anionic regulated electrocatalysts. (a) XRD patterns of LDH-x. (b) Atomic ratio of Ni/Fe and (c) atomic ratio of S/M of LDH-x determined by XPS and EDS, respectively. (d) High-resolution S 2p, O 2p, Fe 2p, and Ni 2p XPS spectra of LDH-x. LDH-10: (e) HAADF-STEM image, (f) the corresponding EDS elemental map, and (g) the linear elemental distribution of the particle marked in (e).

consistent with the XRD results. Considering the stable NiFe cation component and gradually changed sulfur/oxygen anion component, it is concluded that anionic regulation is sufficiently realized by the electrochemical assisted approach to provide hydroxysulfide as a potential electrocatalyst.

High-resolution XPS analysis was further performed to verify the modulated electronic structure of the cation active sites by the surrounding hetero-anionic environment after the electrochemical anionic regulation (Fig. 3d). In accordance with the S/M ratio, high-resolution S 2p XPS spectra exhibit an obvious increase in intensity. The sulfur XPS peaks are identified as typical signals of the sulfur–metal interactions. Meanwhile, the profiles of the O 2p XPS spectra shift to lower binding energies on account of the polarization effect of the substituted sulfur components. Considering sulfur anions with higher polarization degree than oxygen anions, the introduced sulfur anions afford more electrons to the cations and inhibit the electron donation of the original oxygen anions. Therefore, it is rationalized that the oxygen anions receive more electrons and exhibit red-shift in the XPS spectra. This electronic effect of ionic polarization is the same with the modulated transition metal cations. Oxygen anions are hard and have low-polarization, while sulfur anions are soft with a high polarization degree. Substitution of the hydroxyl anions with sulfur anions increases the electronic donation capability of the surrounding anionic environment. Consequently, the sulfur/oxygen hetero-anionic structure endowed by precise anionic regulation shares more electronic interactions with the cations for electronic modulation.38 As demonstrated, despite the negligible change in Fe 2p XPS spectra, the Ni 2p XPS spectra exhibits a red shift.
tendency as expected. The above characterizations unambiguously confirm the precise anionic regulation to construct the desired hetero-anionic structure with maintained morphology, bulk constitution, and modulated electronic structure of the cations. The substituted sulfur anions are atomically dispersed within the hetero-anionic structure to afford NiFe hydroxysulfide as a novel anionic-regulated multi-anion transition metal compound for further applications.

The spatial uniformity of the anionic-regulated NiFe hydroxysulfides was evaluated by EDS elemental mapping. As shown in the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image (Fig. 3e) and the corresponding elemental map (Fig. 3f and Fig. S11, ESI†), the anionic regulated LDH-10 demonstrates uniform distribution of Ni, Fe, O, and S, which is additionally intuitively revealed in the linear scan profile (Fig. 3g). The uniform distribution of the elements without obvious aggregation indicates that the anionic regulation process is uniform and effective for all the hydroxide precursor particles. In summary, the electrochemical anionic regulation approach is ambiguously verified by the precise construction of the oxygen–sulfur hetero-anionic structure from the hydroxide precursor to the targeted hydroxysulfide for further OER and polysulfide electrocatalysis.

To verify the efficiency of the electrochemical anionic regulation strategy and the hydroxysulfide electrocatalysts, the oxygen and sulfur redox electrocatalytic reactivities were evaluated. The OER performance of the anionic regulated electrocatalysts was firstly characterized. Fig. 4a shows the 95% iR-compensated linear sweep voltammetry (LSV) curves of the LDH-x and Ir/C electrocatalysts. The OER electrocatalytic activity enhanced with increased degree of anionic regulation, which is intuitively revealed comparing the overpotential to achieve a current density of 10.0 and 20.0 mA cm$^{-2}$ ($\eta_{10}$ and $\eta_{20}$), respectively (Fig. 4b and Table S2, ESI†). Among all the samples, the LDH-10 electrocatalyst exhibits the best OER electrocatalytic performance with an $\eta_{10}$ of 286 mV and an $\eta_{20}$ of 312 mV. The LDH-10 electrocatalyst even demonstrates better OER electrocatalytic activity than the state-of-the-art Ir/C electrocatalyst. Specifically, the $\eta_{10}$ of the LDH-10 electrocatalyst is 117 mV lower than that of Ir/C electrocatalyst. In addition, the OER electrocatalytic activity of LDH-10 electrocatalyst is outstanding compared with other reported OER electrocatalysts indicating that the electrochemical anionic regulation strategy is highly sufficient to modulate the electronic structure of the cation active sites (Table S3, ESI†). The Tafel plots of LDH-x also show a similar tendency over the degree of anionic regulation (Fig. S12, ESI†), with the regulated electrocatalyst possessing faster kinetics than the pristine LDH-0 electrocatalyst. The electrochemical impedance spectra (EIS) also demonstrates reduced resistance of LDH-x ($x = 1, 5, 10$) over the unregulated LDH-0 (Fig. S13, ESI†). A similar electrochemical active surface area (ECSA) of the LDH-x electrocatalysts additionally excludes the influence of ECSA on the OER performances (Fig. S14, ESI†). Based on these considerations, the regulated anionic structure must be the main reason for the OER electrocatalytic enhancement. The superb OER performances reflect the precise electrochemical assisted anionic regulation which successfully constructed an optimized electronic structure for the active sites for oxygen evolution electrocatalysis. Specifically, the atomically substituted sulfur anions precisely modulate a proper polarization of the cation active sites to balance the conflict between feedstocks adsorption and product desorption, rendering the enhanced OER electrocatalytic performance.

Besides the superb electrocatalytic activity, the LDH-10 electrocatalyst also exhibits remarkable stability to preserve 89.2% of the initial OER current density after a 6.0 h potentiostatic test (Fig. 4c). In comparison, only 59.9% of the current retention is remained for the Ir/C electrocatalyst. A long-term durability test was also performed for the regularly replaced concentrated 1.0 M KOH electrolyte (Fig. S15, ESI†). The LDH-10 electrocatalyst exhibits outstanding stability performance to preserve 95.0 and 81.6% of the initial OER current density after 50 and 100 h durability test, respectively, which surpasses many of the reported electrocatalysts. The excellent stability indicates that the anionic regulated hetero-anionic structure is stable during OER electrocatalysis.

The effectiveness of the electrochemical assisted anionic regulation was additionally verified from the aspect of lithium polysulfide (LiPS) redox electrocatalysis. The LiPS redox reactions are essentially associated with rechargeable Li–S batteries, which includes the conversion between liquid LiPSs and the nucleation of insoluble Li$_2$S from soluble LiPSs. The conversion between liquid LiPSs was evaluated by cyclic voltammetry (CV) tests in symmetric cells. It can be clearly observed that the CV curves of LDH-10 exhibit a higher current response than that of LDH-0 (Fig. 5a), indicating the favorable reactivity of liquid LiPS conversion on the precisely anionic regulated electrocatalyst. Furthermore, the nucleation of Li$_2$S on LDH-0 and LDH-10 electrocatalysts was evaluated. As shown in Fig. 5b, not only does the current of LDH-10 reach its peak 1900 s earlier than LDH-0, but also the maximum current of LDH-10 is 64.1% higher than that of LDH-0. The earlier and higher nucleation current peak demonstrates that the anionic regulated hydroxysulfide effectively promotes the kinetics of Li$_2$S nucleation and increases the deposition capacity.
Electrochemical evaluation of the Li–S battery also verifies the same conclusion (Fig. 5c), for the initial capacity of the LDH-10 battery (1316 mA h g⁻¹) is extraordinarily higher than the capacity of the LDH-0 battery (835 mA h g⁻¹). According to the polarization curves of the initial cycle (Fig. S16, ESI†), LDH-10 also renders the Li–S battery with reduced polarization and lower Li₂S dissolution overpotential than LDH-0, further verifying that LDH-10 is a superior electrocatalyst for LiPS conversion. It has been previously demonstrated that as the cycling duration increases, hydroxysulfide possesses a preferable anion structure than LDH with better electrocatalytic performance. Therefore, in the second cycle, the capacity of the LDH-0 cell increased obviously compared with the LDH-10 cell, consistent with the electrocatalytic performance enhancement via the electrochemical anionic regulation process.

Conclusions

Precise anionic regulation was achieved using the novel electrochemical assisted strategy. The electrochemical assisted approach ensures controllable generation of the regulation reagent, rendering the atomically dispersed extrinsic anions without aggregation. As a result, a novel hetero-anionic structure was realized to modulate the electronic structure of the cation active sites. The resultant hydroxysulfides with accurate hetero-anionic structure were directionally synthesized and exhibited preferable electrocatalytic activities for oxygen and sulfur redox reactions. The OER overpotential at 10.0 mA cm⁻² was reduced to 286 mV, which is much improved over the noble-metal-based Ir/C electrocatalyst. Additional polysulfide electrocatalytic evaluation identifies promoted kinetics on the anionic regulated hydroxysulfides. This work not only provides an effective method towards precise anionic regulation to achieve high-performance electrocatalysts for energy-related processes, but also deepens the understanding of the novel hetero-anionic structure and its electronic interactions in ionic compounds, which could afford advanced materials and reveal unique chemistry.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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