Electrochemically Active Binary Anion Compounds with Tailored Oxygen Vacancy for Energy Storage System

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ABSTRACT.

The search for new materials that exhibit rapid Faradaic energy-storing behavior continues to be ever more important as they offer a promising alternative to battery technology because of their unrivalled ability to deliver large amounts of power along with large amounts of energy. Here, we present a reduced binary anion compound (r-BAC) as a first demonstration of redox-active materials, which are fabricated by a facile and direct activation synthetic method. The r-BAC exhibits excellent energy storage characteristics compared to non-reduced full binary anion compound (f-BAC). Based on the density functional theory (DFT) calculations and the *ex-situ* chemical study, it is found that the superior electrochemical performance is strongly attributed to not only the Ni cation sites ($\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple) that are energetically more activated by oxygen vacancies, but also to the additive electrochemical activity at the unsaturated sulfur sites ($\text{S}^{4+}/\text{S}^{6+}$ redox couple) in a binary anion. Thus, we expect that this study on the binary anion material and the corresponding anion-based charge transfer mechanisms may provide a new strategy for the efficient storage of charge in next-generation energy storage applications.

KEYWORDS. Energy storage system, Faradaic redox reaction; tailored oxygen vacancy; Ni-S-O compound; reduced binary anion.

1. Introduction.

Electrochemical energy storage through extremely efficient Faradaic charge-transfer mechanisms that do not involve the triggering of phase transformations in the electrode materials is expected to be a promising route for energy storage technologies as they offer a means of significantly improving the ability for both storing and delivering large amounts of energy and power over a stable long-term operation [1-5]. Notable improvement in the performance in such devices has been successfully achieved in the large part by developing intrinsically novel redox-active materials and extrinsically complex structures with unique architectures, giving rise to enormous Faradaic charge-transfer reactions [6-8]. Consequently, the ultimate goal of both intrinsic and extrinsic strategies is to optimize the overall charge transfer kinetics, potentially allowing for more efficient charge-storing mechanisms. It has been widely shown that Faradaic mechanisms, which have been employed for their electrochemical energy storage capability, originate through fast and reversible electrosorption and/or intercalation processes with concomitant charge transfer [9-11]. At present, however, most of the research carried out on both the development of new materials and the understanding of the Faradaic charge-transfer mechanisms are generally limited to the transition metal cations of active compound electrodes, which show active electrochemical energy storing kinetics because of their favorable multiple oxidation states [12-15]. However, in principle, atomic anions can also contribute to the electrochemical storage kinetics of active electrode materials due to their various valence (chemical) states.

In recent years, there have been a few studies demonstrating that the energy-storing characteristics of the electrode materials are considerably affected by the modulation of the anion

states through (i) aliovalent doping with anions and (ii) the introduction of anion vacancies, enabling a significant increase in the electrochemical energy storage capability [16-18]. For example, Zhai *et al.* reported that the anion sulfur-doped V_6O_{13-x} electrode shows enhancements in the energy storage capability, resulting from the reversible multiple transformations of vanadium cation states due to the sulfur-doped anion effect [16]. Moreover, the groups of Stevenson and Dunn have reported that the anion (oxygen) vacancies incorporated into the perovskite $LaMnO_3$ and MoO_3 can promote charge storage kinetics of Faradaic redox cation active sites [17,18]. Inspired by the role these anion effects have on the electrochemical behavior, it is believed that tailoring the anion-chemical states could be a viable strategy for exploiting new materials with the feasible chemical states of anions, which can undergo additional Faradaic redox reactions and hence improve the overall electrochemical energy storage through anion-based charge transfer mechanisms. Furthermore, if redox-active materials with a binary anion system could be developed and exploited, would such a new active compound also possess anions with a distinct number of chemical states? Moreover, could this consequently lead to an overall performance enhancement involving synergistically combined effects of the cations and binary anion states through charge-transfer processes? Therefore, this study is aimed not only towards developing new materials based on a binary anion system, but also at gaining an understanding of the anion-mediated Faradaic mechanisms that underpin the overall charge storage process.

In this work, we present a new material candidate consisting of a reduced binary anion compound (r-BAC) as a first proof-of-concept of an electrochemically active electrode. We demonstrate that the r-BAC exhibits excellent charge storage performance through the extra energy-storing contribution that arises from the additional redox-activity of the binary anions, which is attributed to the unsaturated oxidation states of the sulfur that is induced by coupling with

the anion oxygen vacancies in the r-BAC. Moreover, we also investigate the role of the anions in the binary anion compound in terms of the anion-mediated Faradaic charge storage kinetics, which can considerably enhance the overall charge storage properties. An understanding of the novel charge storage mechanism in the binary anion electrode system will offer promising new strategies for future energy storage applications.

2. Results and Discussion

The r-BAC material, grown directly on a 3D microporous Ni foam, was synthesized using a one-step facile liquid-solid chemical oxidation method (Fig. S1). Specifically, a peroxymonosulfuric acid solution was used as the oxidizing agent for the initial activation and formation of the r-BAC (see detailed explanation in the supporting information). The synchrotron high resolution powder X-ray diffraction (HR-XRD) patterns of the r-BAC are shown in Fig. 1a. The XRD pattern was fitted so as to accurately determine the lattice parameters and the crystal structure of the as-synthesized r-BAC samples using a whole-pattern profile matching method [19]. The crystal system of the samples could be modeled as a tetragonal phase with a $P4_12_12$ space group and the lattice parameters of r-BAC obtained from the fits where $a = b = 6.78573(1) \text{ \AA}$ and $c = 18.28561(4) \text{ \AA}$. Interestingly, the diffraction peaks of the r-BAC phase are clearly shifted towards higher angles in 2θ and, representatively, the shift in the main peak (112), $\Delta 2\theta$, is found to be 0.04° as shown in the inset of Fig. 1b, compared to the fully oxidized binary anion compound (f-BAC, Fig. S2) with lattice parameters of $a = b = 6.7993(2) \text{ \AA}$ and $c = 18.3252(7) \text{ \AA}$. Here, it should be noted that, in general, the lattice distortion arising from the crystal defects (e.g. the vacancies) causes a shift in the positions of the XRD peaks. Thus, during the formation process,

the induced oxygen vacancies in the nickel(II) sulfate hexahydrate lattice may lead to a tensile strain along the crystalline lattice, leading to a decrease in the size of the unit cell, which is in good agreement with the results from the DFT lattice calculations (Figs. 1c and S3, and Table S1). Moreover, in addition, we confirmed the formation of the r-BAC by using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) (Fig. 1d) based on a combination of structural and elemental configuration analysis.

To further identify the formation of the r-BAC, we performed XPS analysis to characterize the oxidation states of the r-BAC. It was clearly observed that both the r-BAC and f-BAC samples exhibit two peaks corresponding to binding energies of ~ 856.5 eV and ~ 854.8 eV, representing the Ni^{2+} states associated with the oxidized Ni and sulfur-oxidized Ni states, respectively, as shown in Figs. 2a and 2b [20]. It was also observed that the O 1s XPS spectrum exhibits a main peak at a binding energy of ~ 531.9 eV, corresponding to the sulfur-oxide bonds (Fig. S4). Moreover, interestingly, unlike the S $2p_{3/2}$ spectrum of the f-BAC with only the saturated S^{6+} state (Fig. 2e), it was revealed that the S $2p_{3/2}$ spectrum of r-BAC (Fig. 2b) can be deconvoluted into two different S oxidation states, which are located at binding energies of ~ 168.6 eV and ~ 167.8 eV corresponding to the S^{6+} (Fig. 2f) and S^{4+} (Fig. 2c) states, respectively [20]. These results indicate that there exists a considerable amount of oxygen vacancies in the r-BAC structure, which triggers the unsaturated oxidation states of sulfur, S^{4+} .

In order to address the influence of oxygen vacancies and the unsaturated sulfur oxidation states on the electrochemical kinetic behavior of the r-BAC electrode, the electrochemical features of the redox processes were assessed using a three-electrode system in a 1.0 M KOH electrolyte. As shown in Fig. S5a, the integrated CV area of the r-BAC is much higher than that of the f-BAC, indicating that the electrochemical activity of r-BAC is significantly larger than that of f-BAC. It

is believed that the performance difference between the r-BAC and the f-BAC is closely related to the contribution of unsaturated sulfur oxidation states coupled with the oxygen vacancies. As shown in Fig. S5a and S5e, at the early activation state (1~10 min), two redox humps from Ni and S are clearly observed. After the further reaction time, however, the redox humps of r-BAC are broadened and enlarged, indicating that both S and Ni peaks might be combined in the CV curves. Also, the CV curves of the r-BAC are found to maintain a similar curve profile with increasing scan rates, indicating reversible Faradaic redox behavior (Fig. 3a). Furthermore, the galvanostatic charge/discharge curves indicate that the r-BAC and the f-BAC exhibit a typical battery-like capacitive kinetic with a gentle slope region between 0.2 and 0.4 V (Figs. 3b and S5c).^[21] The calculated energy storage ability of the r-BAC electrode is found to be 11.3 F cm^{-2} (67.4 mAh g^{-1}) at a scan rate of 5 mA cm^{-2} (Fig. 3c), which is considerably higher than previously reported results for Ni-based electrodes and anion oxygen vacancy-controlled electrodes, as summarized in Table S2 and S3, respectively. Remarkably, the r-BAC exhibits a measurably high specific capacity compared to the f-BAC (Figs. 3c and S5d), particularly when considering the overall mass of the r-BAC obtained from inductively-coupled plasma mass spectrometry (ICP-MS) analysis. Notably, the r-BAC can also deliver much higher maximum energy and power densities of 62.8 Wh kg^{-1} and 8882.7 W kg^{-1} , respectively, in comparison with those of the f-BAC. In addition, the r-BAC electrode exhibited stable cycling performance with a high performance retention of 81.7% after 3000 cycling tests (Fig. S6). There are two possible reasons for the performance degradation during cycles. First, the r-BAC utilizes two different atoms (Ni and S) to induce the redox reactions and generate charge. Therefore, the stability of sulfoxide system with Ni atom may be weakened during the oxidation change of sulfur. Second, the thin film structure of r-BAC on the foam might not enough to handle the induced stress during cycling. Accordingly, it is suggested that the

remarkably high performance of the r-BAC is strongly associated with the binary anion configurations consisting of oxygen vacancies and unsaturated sulfur oxidation states. In particular, for the binary anion composition, the partially formed S^{4+} oxidation states might additionally contribute to the improvement of the energy storage ability because these sulfur states can act, electrochemically, as additional redox-reaction sites via Faradaic charge transfer reactions between the unsaturated sulfur atoms and the OH^- ions.

To verify the proposed hypothesis that the unsaturated sulfur states could be the electrochemically active sites, *ex-situ* X-ray photoelectron spectroscopy (XPS) was carried out of the fully-charged (Fig. 3d) and discharged (Fig. 3f) states. When the r-BAC electrode was fully charged, the chemical state of the sulfur-oxidized Ni is transferred from Ni^{2+} to Ni^{3+} due to a redox-reaction with the OH^- ions (the left of Fig. 3e). In contrast, when the device was reverted to the initial discharged state, the charged sulfur-oxidized Ni^{3+} was reduced (the left of Fig. 3g) to Ni^{2+} , exhibiting a reversible redox-behavior during the charge/discharge processes. Most interestingly, we have discovered that unsaturated S^{4+} plays an important role in charge storage. As shown in Fig. S5A, the redox humps of r-BAC are broadened than that of f-BAC, indicating that both S and Ni peaks might be combined in the CV and Ch/Dis curves. As found from the fits in the right of Fig. 3e, the area under the unsaturated S^{4+} curve of the S 2p_{3/2} spectra begins to decline in the fully charged state, whereas the area under the saturated S^{6+} curve is expanded. When the device was subsequently returned to the fully discharged state, the saturated S^{6+} state was returned to the initial, unsaturated S^{4+} state (the right of Fig. 3g). Thus, it is believed that the superb performance of the r-BAC is not only attributed to the active nickel sites, but also to the unsaturated sulfur oxidation states that are in turn modulated by the oxygen vacancies. This Faradaic redox-behavior of the r-BAC can be described through the following reactions:

The Faradaic redox-reaction on the Ni cation can be represented as

For the Faradaic redox-reaction on the unsaturated sulfur oxide anion, this can be represented as

To further reveal and understand the effects of vacancy-mediated binary anions on the redox-reaction kinetics of the r-BAC, we carried out DFT calculations. The most energetically stable (001) surface plane of the r-BAC, which synchronously exposes the Ni and S atoms, was modeled as a periodic slab (Fig. S7). Under the periodic slab, any potential positions of the oxygen atom vacancies were considered and each adsorption energy (E_{OH^-}) of the OH^- on the r-BAC was calculated (Figs. 4 and S8). The DFT calculation results (Figs. 4a and 4b) show that the calculated average E_{OH^-} on the Ni sites with the oxygen vacancies (-2.59 eV) becomes more negative (the adsorption is energetically more favorable) compared to those of the sites with the non-oxygen vacancies (-2.45 eV). This implies that the Ni^{2+} cation with oxygen vacancies has favorable adsorption/reaction kinetics with the OH^- ions. Furthermore, as indicated in Figs. 4c and 4d, the unsaturated sulfur sites in the binary anion system also exhibit a more negative value of the average, E_{OH^-} (-3.41 eV) in comparison with the saturated sulfur sites (-3.31 eV). This finding indicates that the unsaturated sulfur oxide sites on the r-BAC have the capability of adsorbing OH^- ions for storing charge through Faradaic reaction mechanisms. These combined experimental and theoretical results clearly reveal that the unsaturated anion states and the corresponding cation sites in the binary anion composite systems consisting of vacancies play a pivotal role in enhancing the Faradaic reaction kinetics, thereby providing superior electrochemical performance.

3. Conclusions

In summary, we have developed new electrochemically active r-BAC with binary anion configurations as a new family of active Faradaic redox electrode materials, which are synthesized by a facile and direct activation process. The resultant r-BAC electrode exhibited excellent energy storage performance than f-BAC. Based upon the combined experimental and theoretical studies on the anion-mediated electrochemical kinetics, the exceptional performance of r-BAC is attributed to the combined and complementary energy-storing effects of the binary anions with the unsaturated oxidation states that are induced by coupling with the anion oxygen vacancies. These results highlight the possibility of anion-based Faradaic mechanisms for energy storage applications.

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Appendix A. Supporting Information

Additional structural and electrochemical analysis data, and DFT calculation data in Figs. S1-S8 and Table S1-S3.

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Figure Captions

Fig. 1. (a) Synchrotron HR-XRD patterns of r-BAC [red circles: observed profile, black line: calculated profile, and green bar: Bragg positions (tetragonal phase of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)]. (b) The (111), (004), and (112) peaks of the r-BAC (red line) phase with a shift in the peak towards high diffraction angles compared to that of f-BAC (gray line) [The inset indicates the high-resolution XRD pattern of the (112) peak]. (c) The unit cell image of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ optimized by DFT calculations [blue, red, yellow, and pink spheres refer to the Ni, O, S, and H atoms, respectively]. (d) SEM and EDS elemental mapping images of the r-BAC. These results clearly exhibit that Ni, S, and O elements are uniformly distributed on the 3D current collector. All scale bars are 30 μm .

Fig. 2. (a) Ni 2p and (b) S 2p XPS spectra, and (c) structural image of the r-BAC. (d) Ni 2p and (e) S 2p XPS spectra, and (f) structural image of the f-BAC. Blue, red, yellow, and pink spheres indicate the Ni, O, S, and H atoms, respectively.

Fig. 3. (a) CV curves of the r-BAC at different scan rates over the range from 5 to 50 mV s^{-1} . (b) Galvanostatic discharge profiles of the r-BAC at current densities with a range from 5 to 50 mA cm^{-2} . (c) Specific capacity of the r-BAC as a function of the current density. (d) Galvanostatic charge curve of the r-BAC as the fully charged state is approached. (e) The *ex-situ* XPS spectra for Ni 2p (left) and S 2p (right) at the fully charged state. (f) Galvanostatic discharge curve of the r-BAC as the fully discharged state is approached. (g) The *ex-situ* XPS spectra for Ni 2p (left) and S 2p (right) at the fully discharged state.

Fig. 4. (a) Average adsorption energies of the r-BAC and f-BAC at the Ni sites. (b) Structural images of the adsorbed OH^- state on the exposed Ni sites. (c) Average adsorption energies of the r-BAC and the f-BAC at the sulfur oxide sites. (d) Structural images of the adsorbed OH^- state on the exposed S sites. Blue, red, yellow, and pink spheres indicate the Ni, O, S, and H atoms, respectively.

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