Insight of synergistic effect of different active metal ions in layered double hydroxides on their electrochemical behaviors

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A B S T R A C T

Recent years, there have been massive reports of layered double hydroxides (LDHs) used as electrode materials. However, the synergistic effect between different host metal ions on the electrochemical behavior of LDHs is rarely studied. We prepared a series of LDHs with different host metal combinations and investigated their physiochemical properties and redox behaviors to study the synergistic effects between different active metal ions. According to the experimental and theoretical calculation results, LDHs with dual transition metals possessed lower band-gap energies and higher conductivities than mono-transition metal-based samples. The reduced band-gap energy and enhanced conductivity should be ascribed to the hybridization between 3d-orbitals of different transition atoms. As a result, LDHs with dual transition metals exhibited lower charge transfer resistances and redox potentials as well as longer electron lifetime, implying that they could be oxidized or reduced more easily during the redox process. The lowest charge transfer resistance and longest electron lifetime of NiMn-LDHs signify that the synergistic effect between Ni and Mn is the best. From *in situ* X-ray photoelectron spectroscopy results, more than 50% Ni atoms in NiMn-LDHs can be oxidized under 0.45 V, which also demonstrates the excellent redox efficiency of NiMn-LDHs.

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1. Introduction

The impending global environmental issues and energy crisis have prompted intense researches into the development of various types of sustainable energy conversion and storage systems [1–3]. Some important processes to produce and store renewable energy, such as water splitting, oxygen reduction reaction (ORR) and pseudo-supercapacitor, have gained significant attention in the past decades [4–7]. The electrochemical activity of electrode materials is the fundamentality of these energy conversion or storage processes. Recently, layered double hydroxides (LDHs) with a general chemical formula of $\left[M_{1-x}^{2+}M_x^{3+}(OH)_2\right]A_{x/n}^{n-}\cdot mH_2O$ (where M^{2+} is a divalent metal cation, M^{3+} is a trivalent metal cation and A^{n-} is the interlayer anion) has been considered to be the most promising electrochemical electrode material due to its unique lamellar structure with large interlayer spacing. For instance, Zhang et al. [8] synthesized a three-dimensional hierarchical porous flower-like NiAl-LDHs by a liquid-phase deposition method as a high-performance electrode for supercapacitor. With large ion-accessible surface area as well as efficient ion transport pathways, the prepared LDHs electrode achieved a high specific capacity ($1250\,C\,g^{-1}$ at $2\,A\,g^{-1}$) and high cycling stability (76.7% retention after 5000 cycles). Tang et al. [9] also selected NiFe-LDHs-based composites as oxygen evolution reaction (OER) catalysts, which displayed excellent electrocatalytic activity with a small over-potential ($\sim$235 mV in 1 M KOH and $\sim$305 mV in 0.1 M KOH) at a current density of $10\,mA\,cm^{-2}$.

An important structural characteristic of LDHs materials is that the M^{2+} and M^{3+} cations in host layers can be adjusted easily. The composition of LDHs has a big influence on the electrochemical behaviors of LDHs-based electrode materials. For example, Louie et al. [10] prepared a series of Ni-Fe hydroxides and investigated the influence of Fe contents on the redox behavior. They found that Ni-Fe catalysts are significantly more active for oxygen evolution

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reaction (OER) than either Ni or Fe alone. Both redox waves shifted anodically and OER current density decreased in magnitude with increasing Fe content. Similarly, NiCo-LDH presented a much larger energy storage capacity than pristine cobalt hydroxide or nickel hydroxide, which also suggests the higher redox efficiency of the binary LDHs-based electrodes [11]. While the better electrochemical activity of such binary hydroxides has been reported in a number of researches, little is known about the real reason behind this phenomenon. LDHs with different host metal combinations, such as NiAl-LDHs, NiCo-LDHs, NiMn-LDHs and CoMn-LDHs, also displayed different electrochemical behaviors. Sun et al. [12] prepared a class of NiM (M = Fe, Co, Mn) hydroxides nanosheets and studied their electrocatalytic activities. They found that NiFe hydroxides presented the best electrochemical performance. The different electrochemical behaviors of NiM hydroxides were attributed to different Ni-O local environments in $Ni(OH)_2$. Wang et al. [13] also studied the role of different trivalent metal ions in LDHs. They synthesized several LDHs with different metal ions and tested their binding energies and electrochemical behaviors. According to the XPS analyses, they suggested that the different capacitive behaviors should be ascribed to the different frameworks, crystallinities and hydrophilicity of different LDHs. Although some researchers have observed the synergistic effect of different active metal cations in LDHs on the electrochemical behaviors, they just simply ascribed this enhancement of electrochemical performance to the improved nanostructure, crystallinity or conductivity. The change of electronic structure caused by this synergistic effect is rarely mentioned and the intrinsical mechanism of the synergistic effect is still not clear, which limit the further improvement of LDHs-based electrode materials.

Here, in this work, we prepared a series of LDHs materials with different metal combinations in the host layers. The synergistic effect of different active metal ions in LDHs on the physicochemical properties and redox behaviors were systematically investigated. After substitution of other transition metals for Al^{3+}, the band-gap energies of LDHs reduced effectively, giving rise to easier redox reactions for the samples. We also carried out spin-polarized density functional theory (DFT) calculations to further study the difference of electronic structures of the samples. It is found that the electron density distribution and density of states are influenced heavily by the host metal cations combination. The different electronic properties in terms of band-gap energy, electron distribution and density of state at the Fermi level endow the LDHs different electrochemical behaviors during the redox reactions.

2. Experimental section

2.1. Reagents

Nickel (II) nitrate hexahydrate (AR, 98%), cobaltous nitrate hexahydrate (AR, 99%), aluminum nitrate hydrate (AR, 99%) and sodium hydroxide (AR, 96%) were purchased from Aladdin company. Manganese(II) nitrate tetrahydrate (AR, 97%) was purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Synthesis of LDHs materials

LDHs nanoparticles were synthesized via a co-precipitation-hydrothermal method. Briefly, a mixture of 0.7 M $Ni(NO_3)_2$ and 0.3 M $Al(NO_3)_3$ solution (15 mL) was quickly added to 50 mL of 0.45 M NaOH solution under vigorous stirring. After stirring for 10 min, the LDHs slurry was collected, washed, and then re-

suspended in 40 mL deionized water. The inhomogeneous suspension was transferred to an autoclave and heated in an oven at 100 °C for 16 h. After hydrothermal treatment, a transparent and homogenous LDHs suspension was obtained. The sample was then collected by centrifugation and labeled as NiAl-LDHs. CoAl-LDHs, MnAl-LDHs, CoMn-LDHs, NiCo-LDHs and NiMn-LDHs were also synthesized with the same procedures.

2.3. Characterizations

The samples were characterized by X-ray diffraction (XRD, X'pert PRO MPD with Cu Ka radiation, λ = 0.15406 nm) and scanning electron microscopy (SEM, S-4800Hitachi) for structure and morphologies detection. Fourier transform infrared spectroscopy (FTIR, Nicolet 6700) and X-ray photoelectron spectroscopy (XPS) were used to assess the surface composition and chemical state of the samples. The XPS measurements were carried out on PHI-5000 Versa Probe spectrometer equipped with monochromatized Al-Kα radiation (1486.6 eV). The oxidability of the samples was studied by temperature programmed oxidation analysis. The oxidation process was performed from room temperature to 800 °C with a heating rate of 10 °C/min. The optical absorption spectra were recorded by a UV–vis spectrometer (UV-2600, Shimadzu, Japan) over the range of 300–800 nm.

2.4. Computational methods

To support the experimental observations, we have also performed spin-polarized density functional theory (DFT) calculations by using Materials Studio version 7.0 software package (Accelrys Software Inc.:San Diego, CA) [14]. The space groups of all these LDHs are R3m, with unit cell parameters α = β = 90°, and γ = 120° [15]. The other three unit cell parameters, a, b (ranging from 3.02 to 3.07 Å for a and b) and c (22.12 to 22.67 Å) are calculated from the XRD data of these LDHs. The molar ratio of M^{2+} to M^{3+} is set to be 3, constructing the LDHs supercell by 4 × 4 × 1 in the a-, b- and c- directions.

2.5. Electrochemical measurement

The composites were mixed with carbon black as a conductive additive and polytetrafluoroethylene as a binder at a weight ratio of 85:10:5. After drying at 100 °C for 12 h, the mixture was smeared on a nickel foam and pressed at 100 kg/cm^2 to form a slice as a working electrode. The nickel foam was pretreated sequentially with acetone, 2 M HCl solution, deionized water and absolute ethanol, to clean their surfaces and eliminate thin surface oxide layer. The loading amount of active materials for a single electrode was 2 mg. The electrochemical performances of the LDHs materials were evaluated in a 1 M KOH solution. All electrochemical measurements including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in a three-electrode system using a platinum film as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. CV tests were performed between 0 V and 0.45 V (vs. SCE) at different scanning rates. EIS were tested at frequencies ranging from 0.01 to 10^5 Hz.

3. Results and discussion

3.1. LDHs with one transition metal in host layers

3.1.1. Structure and surface properties
NiAl-LDHs, CoAl-LDHs and MnAl-LDHs with single transition metal in host layers were firstly prepared and collectively referred