

高熵($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O 纳米粉体的简易制备及超电容性能

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摘 要: 高熵氧化物是一种由高构型熵稳定的新型材料, 有望具有独特的电化学性能。采用聚丙烯酰胺凝胶法制备了($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O 纳米粉体并研究了其超级电容性能。结果表明: 单相($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O 纳米粉体的制备温度随着丙烯酰胺/金属阳离子摩尔比的增加而降低。当丙烯酰胺/金属阳离子摩尔比为 120:1 时, 在 900 °C 煅烧 2 h 所制备的岩盐相高熵纳米粉体呈现出球形形态, 粒径为 40~65 nm。该高熵纳米粉体在 1 A/g 的电流密度下具有 402 F/g 的比电容; 当电流密度增大到 20 A/g 时, 仍然能保持 62% 的初始比电容; 在电流密度为 5 A/g 时, 经过 2 000 次充放电循环后, 电容保持率为 61%, 该研究表明高熵($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O 纳米粉体在超级电容器电极材料领域具有良好的应用前景。

关键词: 高熵氧化物; 聚丙烯酰胺; 超级电容器; 电化学性能; 电极材料

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Facile Synthesis of High-Entropy ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O Nanopowder and Its Electrochemical Properties As Supercapacitor Electrode

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Abstract: High-entropy oxides (HEO) are a novel material with the unique electrochemical properties, which are stabilized due to the high configurational entropy. In this paper, a high-entropy ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O nanopowder with the sizes of 40–65 nm and a rocksalt structure was synthesized by a polyacrylamide gel method and subsequent calcination at 900 °C for 2 h in the presence of a mole ratio of acrylamide/metal cations of 120:1. The results show that the temperature of forming a single-phase ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O nanopowder decreases with the increase of the mole ratio of acrylamide/metal cations. The HEO nanopowder has a specific capacitance of 402 F/g at a current density of 1 A/g. A rate capability of 62% appears at 20 A/g. The capacitance retention is 61% after 2 000 cycles at a current density of 5 A/g. It is indicated that ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O nanopowder could be used as a prospective electrode material for supercapacitors.

Keywords: high-entropy oxides; acrylamide; supercapacitors; electrochemical properties; electrode materials

1 Introduction

Supercapacitors (SCs) have attracted recent attentions as one of the most promising energy storage devices because of their fast charge-discharge rate, excellent reversibility, high power density, superior cycling stability, wide range of operating temperatures, safe operation and environmental friendliness^[1-4]. These

unique characteristics enable SCs to be excellent candidates for electronic devices and industrial applications. However, the energy densities of SCs are lower than that of the batteries. Increasing the capacitance (C) or cell voltage (V) is an effective approach to improve the energy density (E) of SCs as $E=0.5CV^2$. In this context, intensive studies have been done to explore the electrode materials with a large specific capacitance.

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Many electrode materials have been developed for SCs, such as carbon materials^[5–6], oxides^[7], sulfides^[8], nitrides^[9–10], MXene^[11], MOF^[12], and composites^[13–16]. However, developing the ideal electrode materials for SCs with the supreme performances (*i.e.*, high energy density, high power density, high conductivity, and long-term charge–discharge cycling stability) is still a challenge^[17]. It is thus desirable for the practical application of SCs in industry to investigate and develop advanced electrode materials.

High-entropy materials have attracted great attentions due to the high entropy effect, sluggish diffusion effect, severe lattice distortion, and cocktail effect^[18–22]. These materials comprise the incorporation of multiple elements into single-phase crystal structures, which are stabilized by the high configurational entropy. High-entropy materials provide a huge amount of possibilities in composition design and property tailoring paradigms. Recent studies demonstrate that high-entropy oxides (HEOs) possess notable advantages in terms of their electrochemical properties such as capacity retention, Li-ion conductivity, and cycling stability^[23–26]. Sarkar *et al.* found that high-entropy (CoCuMgNiZn)O used as conversion-based electrode material could be cycled for over 500 times without significant capacity degradation at a specific current of 200 mA/g^[23]. Chen *et al.* reported that (MgTiZnCuFe)₃O₄ particles as anodes for lithium ion batteries delivered a large reversible capacity of 504 mA·h/g at 100 mA/g after 300 cycles, and an exceptional rate capacity of 272 mA·h/g at 2 000 mA/g^[24]. Bérardan *et al.* reported that the (MgCoNiCuZn)_{1–x–y}Ga_yLi_xO displayed a high Li⁺ conductivity of over 10^{–3} S/cm at room temperature^[25]. Liu *et al.* reported that (LiMgCoNiCuZn)O was applied as a anode materials for lithium ion batteries, which achieved a high capacity retention of 83% after 300 cycles at 1 A/g^[26]. However, the use of HEOs in SCs have not been extensively investigated yet.

To better utilize the HEOs in SCs, the HEOs should be synthesized to nanopowders, which can offer abundant active sites for Faradic redox reactions and short pathways for charge transportation^[27]. However, it is rather difficult to prepare the HEOs nanopowder by conventional solid-state method because high temperature and long holding time in calcination cause severe grain coarsening and particle agglomeration. Recent methods have been developed to synthesize high-entropy ceramic nanopowders, such as flame spray pyrolysis^[28], polymer derived ceramics route^[29], solution combustion synthesis^[30–31], and ultrasonication-based method^[32]. In spite of the advantages of these methods, some of them have disadvantages, *i.e.*, requirement of complicated equipment, use of expensive organic salt and surfactant, and long reaction time. It is therefore imperative to develop simple and cost-effective strategies to prepare HEOs nanopowders for their application in SCs.

Polyacrylamide gel method is an innovative nanoparticle preparation method that allows components to be mixed evenly at the atomic level. This method is simple, time saving, and allows for accurate control of the stoichiometric ratio of the samples. Furthermore, the original materials used in the polyacrylamide gel method are inorganic salts^[33–34].

This paper was to prepare a ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O nanopowder by a facile polyacrylamide gel method and subsequent calcination. In addition, the electrochemical properties of the nanopowder as a supercapacitor electrode were also analyzed.

2 Experimental

2.1 Preparation procedure

The raw materials of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Macklin Chemical, China) were dissolved in deionized water to obtain a solution. The concentration of $\text{Mg}^{2+}/\text{Co}^{2+}/\text{Ni}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$ was 0.04 mol/L. Afterwards, acrylamide, N-N'-methylene-bis-acrylamide, and ammonium persulfate at a mole ratio of 24:2:1 were added in the solution. The mole ratio of acrylamide/metal cations (abbreviated as A/M) was adjusted to 50:1, 80:1, and 120:1, respectively. A clear mixed solution was obtained after a vigorous stirring for 60 min. Subsequently, the mixed solution was heated in a water bath at 80 °C until a wet gel was formed. The wet gel was dried in an oven at 80 °C for 2 d to form xerogel. The xerogel was calcined at 700–1 000 °C for 2 h, finally obtaining a high-entropy ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O nanopowder.

2.2 Characterizations

The phase composition of the sample was characterized by a model D8 X-ray diffractometer (XRD, Bruker, Germany). The morphology of HEO nanopowders was observed by a model S-4800 field-emission scanning electron microscope (FESEM, Hitachi Co., Ltd., Japan). The microstructure and chemical composition of HEO nanopowders were examined by a model 2100F transmission electron microscope (TEM, JEOL Co., Japan) equipped with energy dispersive X-ray spectroscopy (EDS). The X-ray photoelectron spectra (XPS) were determined by a model VG ESCALab 250 X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA).

The electrochemical properties of high-entropy HEO nanopowders were analyzed in a three compartment cell using a model CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China). Platinum plate (1 cm×1 cm) was used as a counter electrode, while a saturated calomel electrode (SCE) was used as a reference electrode. Working electrode was fabricated by coating the well-mixed slurry of HEO nanopowders, acetylene black and polytetrafluoroethylene (PTFE, aqueous solution) in a mass ratio of 8:1:1 on nickel foam (1 cm×1 cm), and

then vacuum drying at 60 °C for overnight. The mass loading of HEO nanopowders on nickel foam was approximately 1.2 mg/cm². The electrolyte was 6 mol/L KOH aqueous solution. The measurement methods include cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests.

The specific capacitance was calculated from GCD curve by^[35–36]

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where C_s , I , Δt , m , and ΔV are the specific capacitance (F/g), discharge current (A), discharge time (s), mass of active material (g), and discharging potential range (V), respectively.

3 Results and discussion

Fig. 1 shows the XRD patterns of powders synthesized *via* calcination of xerogel with different A/M mole ratios at 700–1 000 °C for 2 h.

In Fig. 1(a), for the sample obtained at 700 °C, the diffraction peaks as $2\theta = 36.82^\circ$, 42.77° , 61.94° , 74.44° and 78.26° can be indexed as the reflections of planes (111), (200), (220), (311) and (222) from a rocksalt phase. In addition, the diffraction peaks corresponding to spinel Co₃O₄ (JCPDS 42–1467), wurtzite ZnO (JCPDS 36–1451), and tenorite CuO (JCPDS 02–1040) appear. The diffraction peaks corresponding to the spinel Co₃O₄, wurtzite ZnO, and tenorite CuO gradually disappear as the calcination temperature increases. For the sample obtained at 1 000 °C, the XRD pattern contains only the diffraction peaks of rocksalt phase, indicating that a single-phase solid solution with a rocksalt structure is formed.

Fig. 1(b) and Fig. 1(c) shows the XRD patterns of powders synthesized *via* calcination of xerogel with the A/M mole ratios of 80:1 and 120:1 at 700–1 000 °C for 2 h, respectively. Clearly, the formation temperature of single-phase HEO decreases with the increase of the A/M mole ratio.

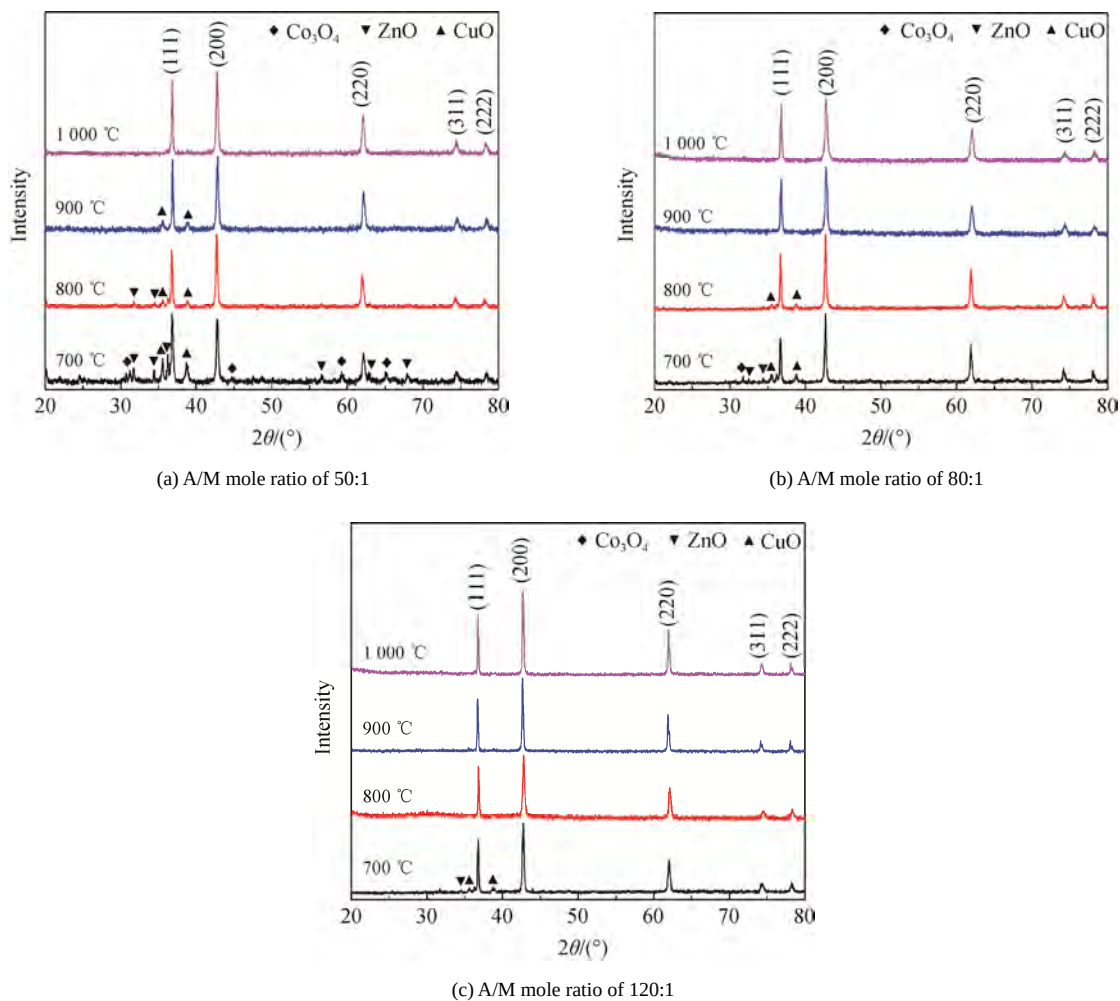


Fig. 1 XRD patterns of HEO powders synthesized *via* calcination of xerogels with different A/M mole ratios at 700–1 000 °C for 2 h

It is indicated that the A/M mole ratio has a great effect on the formation temperature of HEO with a rocksalt structure. A greater A/M mole ratio is beneficial

to synthesize the HEO nanopowder at lower temperatures. In general, the synthesis of HEO always requires high temperatures to mix and stabilize the

multiple elements with different atomic radii, valences, and oxidation potentials^[28, 37]. In this work, a high-entropy ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O nanopowder can be synthesized at a lower temperature (*i.e.*, 800 °C), which is probably due to the intimate mixing of metal elements via the polyacrylamide gel method.

Fig. 2 shows the schematic illustration of synthesis of HEO nanopowder by a polyacrylamide gel method and subsequent calcination. Clearly, the starting metal salts, acrylamide (AM), and N-N'-methylene-bis-acrylamide (MBAM) are uniformly mixed in a solution. The polymerization of AM and MBAM occurs under the action of initiator ammonium persulfate after heating at 80 °C, resulting in a complex network with inter connected loops and branches^[33–34].

As a result, the metal salts are immobilized uniformly in the confined micro-space formed by the polymerization, which allows metal salts to be mixed evenly in an atomic level. Moreover, the confined micro-space ensures the shortened element diffusion distance, which can prevent the phase segregation and reduce the synthesis temperature. A greater A/M mole ratio can lead to the smaller micro-space, which ensures a shortened element diffusion distance, thus promoting the reaction kinetics. Consequently, the formation temperature of HEO decreases with the increase of A/M mole ratio (see Fig. 1). In addition, the polyacrylamide gel method is simple and easily operated, which provides a facile approach to synthesize the HEO nanopowders.

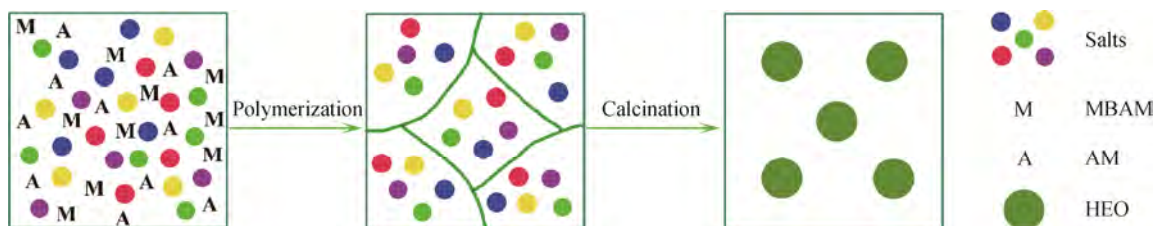
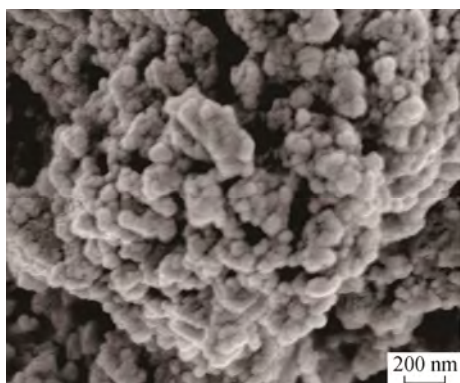


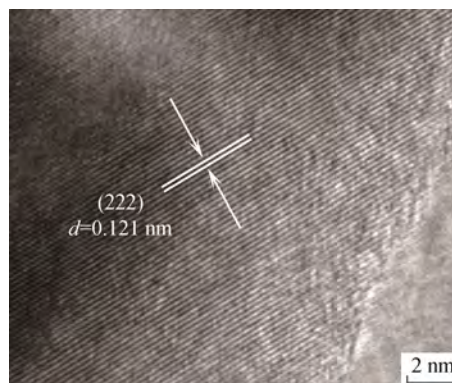
Fig. 2 Schematic illustration of synthesis of HEO nanopowder by a polyacrylamide gel method and subsequent calcination

Fig. 3 shows the SEM image, high-resolution TEM image and TEM image–EDS elemental mapping profiles

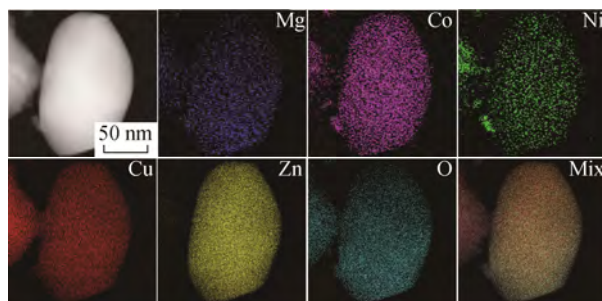
of HEO nanopowder synthesized via calcination of xerogel with an A/M mole ratio of 120:1 at 900 °C for 2 h.



(a) SEM image



(b) High-resolution TEM image



(c) TEM-EDS results

Fig. 3 SEM image, high-resolution TEM image and TEM image–EDS elemental mapping profiles of HEO nanopowder synthesized via calcination of xerogel with an A/M mole ratio of 120/1 at 900 °C for 2 h

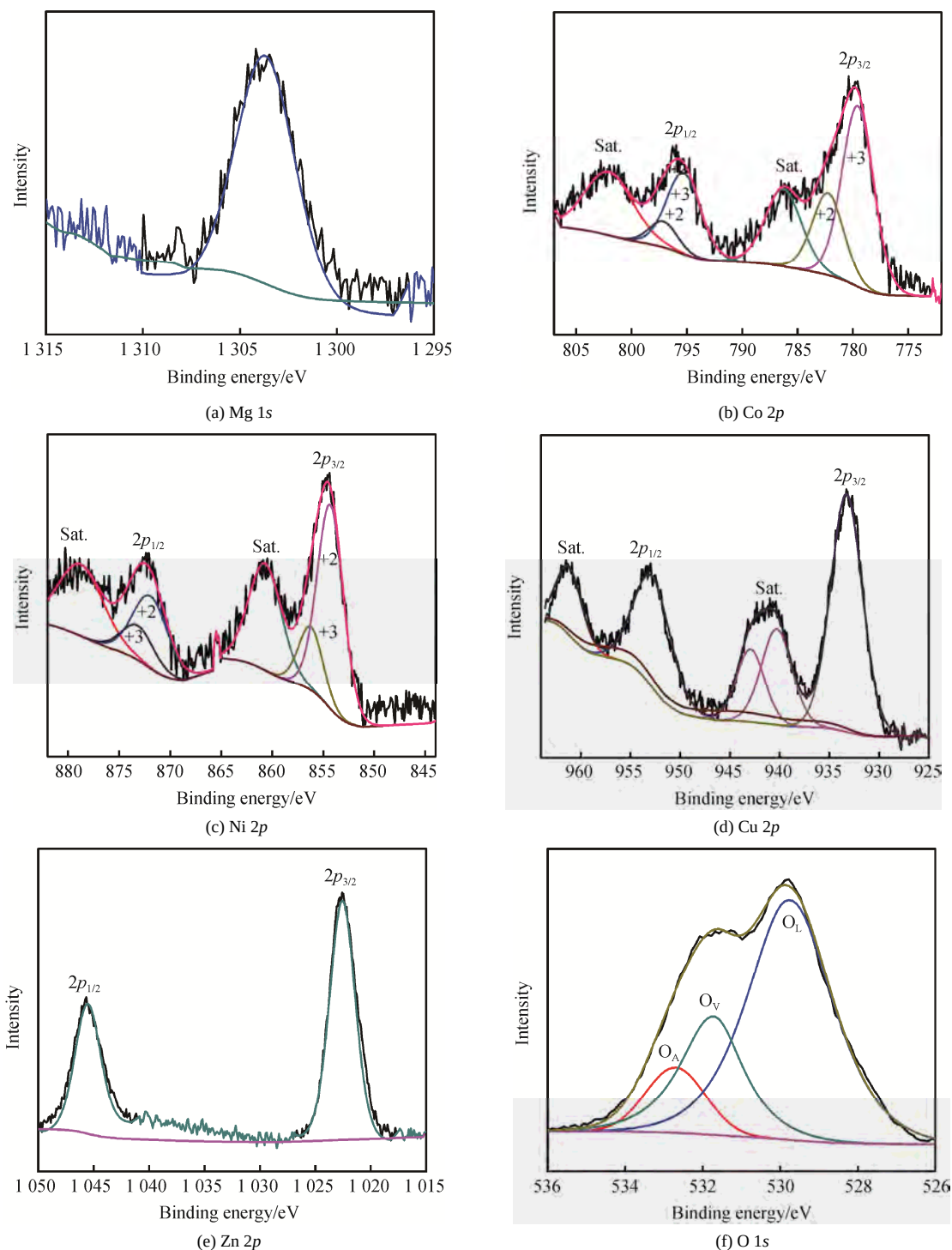
In Fig. 3(a), the HEO nanoparticles in the powder exhibit a spherical morphology with the sizes of 40–65 nm.

In Fig. 3(b), the clear and sharp lattice fringe indicates the high crystallinity and homogeneous distribution of

elements in an atom scale. Also, the measured lattice fringe of 0.121 nm corresponds well to the typical inter-planar spacing of the plane (222) of HEO particle with a rocksalt structure. In Fig. 3(c), the elements are homogeneously distributed throughout the particle.

Fig. 4 shows the high-resolution XPS spectra of HEO nanopowder synthesized *via* calcination of xerogel with an A/M mole ratio of 120:1 at 900 °C. In Fig. 4(a) and Fig. 4(e), clearly, the XPS spectra of elements Mg

and Zn reveal that Mg and Zn cations in the HEO nanopowder are at a valence of +2 state^[38–39]. For the XPS spectrum of Cu, the intense shake-up satellite peaks at 940 and 943 eV are related to Cu²⁺^[40], indicating that Cu cations exist in the form of +2 state in the HEO nanopowder. In Fig. 4(b), the $2p_{1/2}$ and $2p_{3/2}$ energy states locate at 795.94 and 779.89 eV, respectively, with an energy splitting of 16.05 eV. The deconvoluted bands at 711.97 and 725.11 eV are assigned to Co²⁺ oxidation state, while the bands at



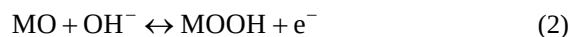
Sat. is satellite.

Fig. 4 High-resolution XPS spectra of HEO nanopowder synthesized *via* calcination of xerogel with an A/M mole ratio of 120:1 at 900 °C

779.58 and 795.37 eV are attributed to Co^{3+} ^[15]. In Fig. 4(c), $2p_{1/2}$ and $2p_{3/2}$ energy states locate at 872.64 and 854.69 eV, respectively, with an energy splitting of 17.95 eV. The deconvoluted peaks at 854.48 and 872.24 eV belong to the Ni^{2+} oxidation state, and the peaks at 856.45 and 873.4 eV are associated with Ni^{3+} oxidation state^[41]. In Fig. 4(b) and Fig. 4(c), Co and Ni exist in various valence states of +2 and +3. These multiple valence oxidation states of elements can promote the capacitance of electrode materials due to the multi-electron transfer redox reactions. In Fig. 4(f), three Gaussian peaks at 529.78, 531.74, and 532.75 correspond to the lattice oxygen (O_L), oxygen vacancy (O_V), and adsorbed oxygen (O_A), respectively^[26, 42]. According to the peak area ratio, it can be evaluated that the HEO nanopowder has a higher proportion of oxygen vacancy. Oxygen vacancies increase the equilibrium electron density, thereby improving the electrical conductivity^[43]. In addition, oxygen vacancies can serve as electroactive centers to facilitate redox reactions^[44]. Therefore, the presence of oxygen vacancies is beneficial to the electrochemical properties of HEO nanopowder.

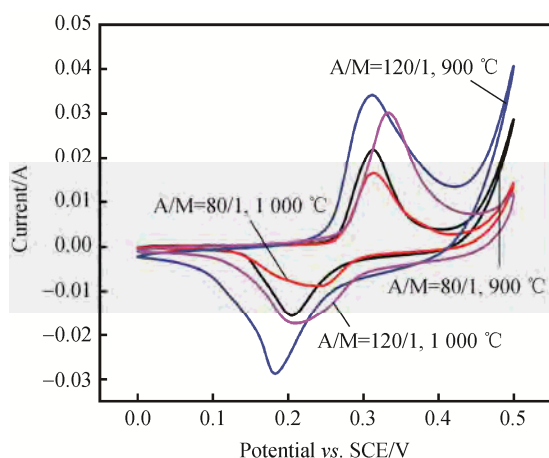
Fig. 5 shows the CV and GCD curves of HEO nanopowders synthesized under different experimental

conditions in a potential range of 0–0.5 V at a scan rate of 5 mV/s. In Fig. 5(a), the symmetric redox peaks caused by the Faradic redox reactions appear for all the samples. The Co and Ni elements contained in HEO nanopowder have variable oxidation states, which favour the Faradic redox reactions. The most plausible reactions in alkaline electrolyte can be described as^[42, 45]

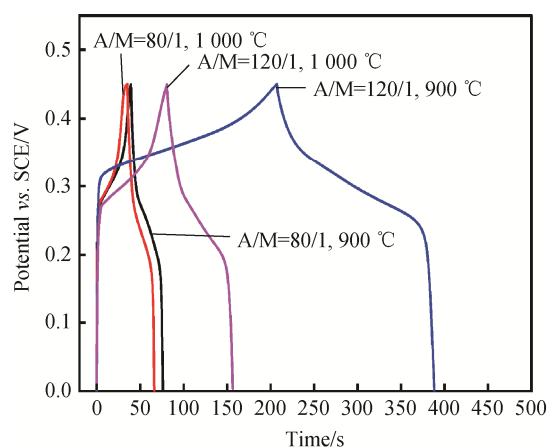


where M represents the metal elements. Moreover, it can be observed that the HEO nanopowder obtained via calcination of xerogel at an A/M mole ratio of 120:1 at 900 °C has the maximum CV integral area, implying the largest specific capacitance among all the samples.

In Fig. 5(b), the HEO nanopowder obtained via calcination of xerogel at an A/M mole ratio of 120:1 at 900 °C has the longest discharge time, further confirming the largest specific capacitance among these samples. According to Eq. (1), the specific capacitances of HEO nanopowders obtained at A/M ratio of 80:1 and 900 °C, A/M ratio of 80:1 and 1 000 °C, A/M ratio of 120:1 and 900 °C, and A/M ratio of 120:1 and 1 000 °C were calculated to be 81, 68, 402, and 168 F/g, respectively, at a current density of 1 A/g.



(a) CV curves at a scan rate of 5 mV/s



(b) GCD curves at a current density of 1 A/g

Fig. 5 CV and GCD curves of HEO nanopowders synthesized under different experimental conditions

Fig. 6 shows the CV curves of HEO nanopowders at different scan rates and the GCD curves of HEO nanopowders at different current densities, respectively. In Fig. 6(a), the oxidation and reduction peaks displayed in the CV curves indicate the pseudo-capacitance feature^[46–47]. The positions of oxidation and reduction peaks shift to higher and lower potentials, respectively, as the scan rate increases, which can be ascribed to the polarization effect and irreversible Faradic redox reactions^[15, 48]. Moreover, the CV curves retain a similar shape at various scan rates, even as the scan rate increases to 100 mV/s. This result implies the good electrochemical reversibility of electrode. In addition, the

peak current increases with the increase of the scan rate, indicating the fast kinetic of Faradic redox reactions^[49]. In Fig. 6(b), all the GCD curves exhibit plateaus regions in the potential between 0.32 and 0.45 V, originating from the reversible Faradic redox reactions^[36]. These results further verify the pseudo-capacitance feature of electrode material. Furthermore, all the GCD curves are almost symmetrical at different current densities, further revealing a good electrochemical reversibility of electrode material^[50]. According to the GCD curves, the specific capacitances at current density of 1, 2, 3, 5, 10, and 20 A/g were calculated to be 402, 376, 357, 332, 296, and 249 F/g, respectively.

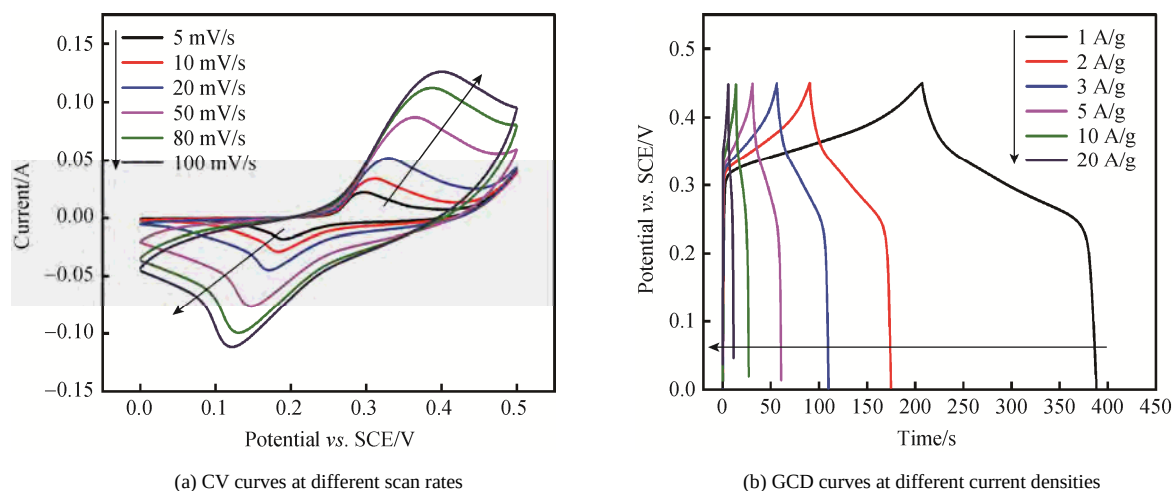


Fig. 6 CV and GCD curves of HEO nanopowders

Fig. 7 shows the rate capability, cycling performance, and electrochemical impedance spectrum of HEO nanopowder. In Fig. 7(a), the capacitance retention decreases with the increase of current density. This is due to the fact that the Faradic redox reaction is a diffusion process. The active sites for the Faraday reaction are not fully utilized at a large current density^[45]. The HEO nanopowder exhibits a relatively high rate capability of

62% from 1 to 20 A/g, which is important for practical application of SCs. In Fig. 7(b), the HEO nanopowder retains 61% of its initial specific capacitance after 2000 continuous GCD cycles. The reason of the capacity fading is not rather clear. It is proposed that the decrease of specific capacitance after the long-term cycling could be mainly due to the abscission of the active material from Ni foam. During the charge–discharge cycling,

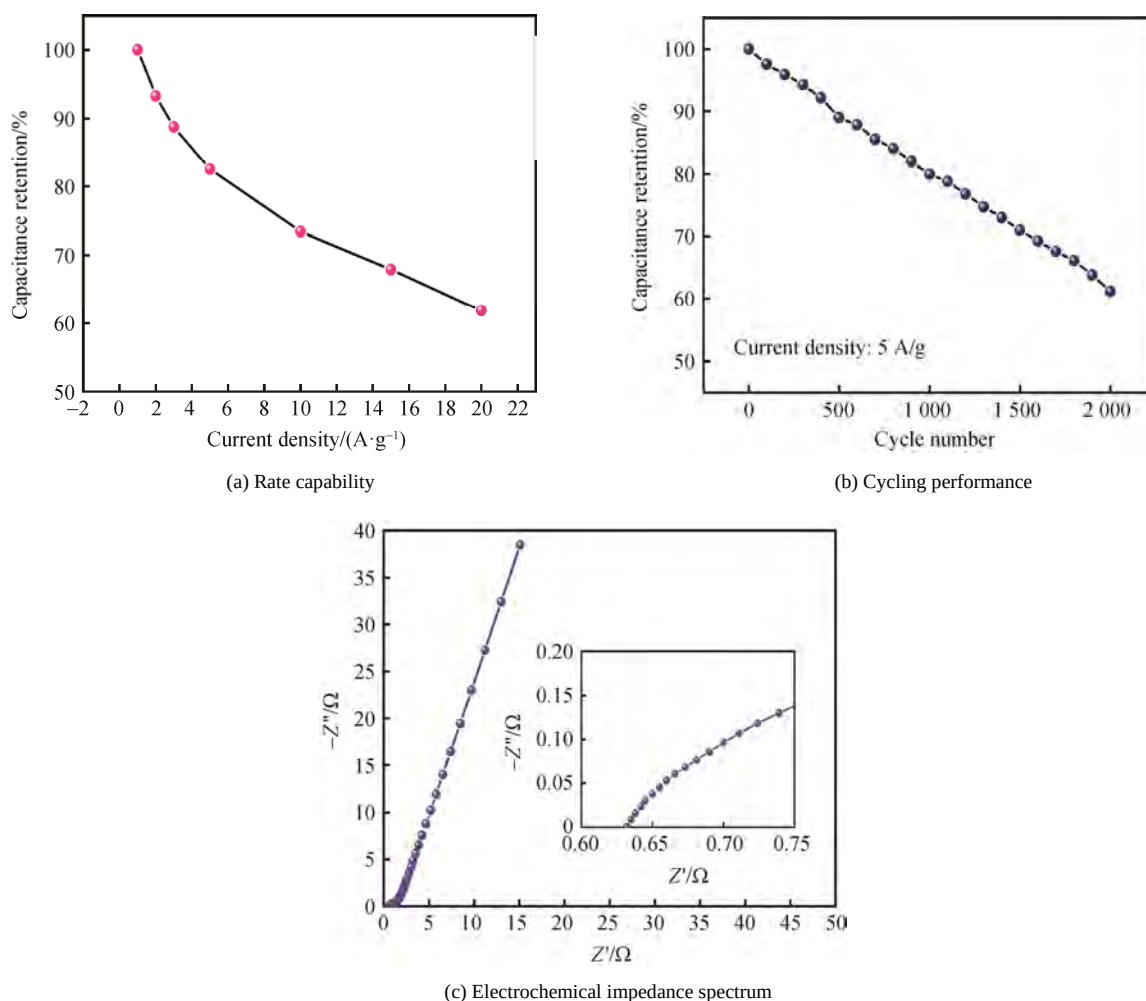


Fig. 7 Rate capability, cycling performance, and electrochemical impedance spectrum of HEO nanopowder

transition metal oxide particles begin to agglomerate, and then the secondary particles agglomerate, resulting in the formation of the penetrating cracks. The crack propagation may lead to the loss of active material from current collector.

In Fig. 7(c), the slope of the linear plot at low frequency means the Warburg impedance value (R_w), which is related to the ion diffusion within electrodes^[50]. The large slope of the straight line in the low-frequency range implies the low R_w value of electrode. In addition, the intersection with the real axis stands for the series resistance (R_s), which is composed of the intrinsic resistance of the electrode materials, the ionic resistance of the electrolyte and the ohmic resistance of the interface between the electrode and current collector^[50]. As is depicted in the inset of Fig. 7(c), HEO nanopowder has a low R_s of $0.63\ \Omega$. The low R_w and R_s conclusively lead to the good conductivity and rapid ion transport kinetics for HEO nanopowder.

4 Conclusions

A high-entropy ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$) (HEO) nanopowder with the sizes of 40–65 nm and the rocksalt structure was synthesized by a polyacrylamide gel method and subsequent calcination at $900\ ^\circ\text{C}$ for 2 h in the presence of an A/M ratio of 120:1. The mole ratio of A/M for the synthesis had an influence on the phase transformation. The HEO nanopowder showed a capacitance of 402 F/g at a current density of 1 A/g. A rate capability of 62% appeared at 1–20 A/g. The capacitance retention was 61% after 2 000 cycles at a current density of 5 A/g. It was indicated that the ($\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$) nanopowder could be used as a prospective electrode material for SCs.

参考文献:

- [1] SHAO Y, EL-KADY M F, SUN J, et al. Design and mechanisms of asymmetric supercapacitors[J]. *Chem Rev*, 2018, 118: 9233–9280.
- [2] ZHU Q, ZHAO D, CHENG M, et al. A new view of supercapacitors: Integrated supercapacitors[J]. *Adv Energy Mater*, 2019, 9: 1901081.
- [3] POONAM, SHARMA K, ARORA A, et al. Review of supercapacitors: Materials and devices[J]. *J Energy Storage*, 2019, 21: 801–825.
- [4] GONZÁLEZ A, GOIKOLEA E, BARRENA J A, et al. Review on supercapacitors: Technologies and materials[J]. *Renew Sustain Energy Rev*, 2016, 58: 1189–1206.
- [5] CHEN T, DAI L. Carbon nanomaterials for high-performance supercapacitors[J]. *Mater Today*, 2013, 16: 272–280.
- [6] SUN P, ZHANG S, BI H, et al. Tuning nitrogen species and content in carbon materials through constructing variable structures for supercapacitors[J]. *J Inorg Mater*, 2021, 36: 766–772.
- [7] AN C, ZHANG Y, GUO H, et al. Metal oxide-based supercapacitors: Progress and perspectives[J]. *Nanoscale Adv*, 2019, 1: 4644–4658.
- [8] BARIK R, INGOLE P P. Challenges and prospects of metal sulfide materials for supercapacitors[J]. *Curr Opin Electrochem*, 2020, 21: 327–334.
- [9] LIU X, ZANG W, GUAN C, et al. Ni-doped cobalt-cobalt nitride heterostructure arrays for high-power supercapacitors[J]. *ACS Energy Lett*, 2018, 3: 2462–2469.
- [10] WEI B, MING F, LIANG H, et al. All nitride asymmetric supercapacitors of niobium titanium nitride-vanadium nitride[J]. *J Power Sources*, 2021, 481: 228842.
- [11] YANG J, BAO W, JAUMAUX P, et al. MXene-based composites: Synthesis and applications in rechargeable batteries and supercapacitors[J]. *Adv Mater Interfaces*, 2019, 6: 1802004.
- [12] DAI F, WANG X, ZHENG S, et al. Toward high-performance and flexible all-solid-state micro-supercapacitors: MOF bulk vs. MOF nanosheets[J]. *Chem Eng J*, 2021, 413: 127520.
- [13] ZHENG Z, WU W, YANG T, et al. *In situ* reduced MXene/AuNPs composite toward enhanced charging/discharging and specific capacitance[J]. *J Adv Ceram*, 2022, 11: 742–753.
- [14] XU J, YANG N, HEUSER S, et al. Achieving ultrahigh energy densities of supercapacitors with porous titanium carbide/boron-doped diamond composite electrodes[J]. *Adv Energy Mater*, 2019, 9: 1803623.
- [15] HAN C, XU X, MU H, et al. Construction of hierarchical sea urchin-like manganese substituted nickel cobaltite@tricobalt tetraoxide core-shell microspheres on nickel foam as binder-free electrodes for high performance supercapacitors[J]. *J Colloid Interface Sci*, 2021, 596: 89–99.
- [16] CHENG Y, ZHANG Y, MENG C. Template fabrication of amorphous Co_2SiO_4 nanobelts/graphene oxide composites with enhanced electrochemical performances for hybrid supercapacitors[J]. *ACS Appl Energy Mater*, 2019, 2: 3830–3839.
- [17] HUSSAIN I, LAMIEL C, AHMAD M, et al. High entropy alloys as electrode material for supercapacitors: A review[J]. *J Energy Storage*, 2021, 44: 103405.
- [18] YEH J W, CHEN S K, LIN S J, et al. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes[J]. *Adv Eng Mater*, 2004, 6: 299–303.
- [19] CANTOR B, CHANG I, KNIGHT P, et al. Microstructural development in equiatomic multicomponent alloys[J]. *Mater Sci Eng A*, 2004, 375: 213–218.
- [20] ROST C M, SACHET E, BORMAN T, et al. Entropy-stabilized oxides[J]. *Nat Commun*, 2015, 6: 8485.
- [21] XIANG H, XING Y, DAI F, et al. High-entropy ceramics: Present status, challenges, and a look forward[J]. *J Adv Ceram*, 2021, 10: 385–441.
- [22] OSES C, TOHER C, CURTAROLO S. High-entropy ceramics[J]. *Nat Rev Mater*, 2020, 5: 295–309.
- [23] SARKAR A, VELASCO L, WANG D, et al. High entropy oxides for reversible energy storage[J]. *Nat Commun*, 2018, 9: 3400.
- [24] CHEN H, QIU N, WU B, et al. A new spinel high-entropy oxide ($\text{Mg}_{0.2}\text{Ti}_{0.2}\text{Zn}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2}\text{O}_4$) with fast reaction kinetics and excellent stability as an anode material for lithium ion batteries[J]. *RSC Adv*, 2020, 10: 9736–9744.
- [25] BÉRARDAN D, FRANGER S, MEENA A K, et al. Room temperature lithium superionic conductivity in high entropy oxides[J]. *J Mater Chem A*, 2016, 4: 9536–9541.
- [26] LIU X, XING Y, XU K, et al. Kinetically accelerated lithium storage in high-entropy (LiMgCoNiCuZnO) enabled by oxygen vacancies[J]. *Small*, 2022, 18: 2200524.
- [27] MA Y, MA Y, WANG Q, et al. High-entropy energy materials:

- Challenges and new opportunities[J]. *Energy Environ Sci*, 2021, 14: 2883–2905.
- [28] SARKAR A, DJENADIC R, USHARANI N J, et al. Nanocrystalline multicomponent entropy stabilised transition metaloxides[J]. *J Eur Ceram Soc*, 2017, 37: 747–754.
- [29] MA M, SUN Y, WU Y, et al. Nanocrystalline high-entropy carbide ceramics with improved mechanical properties[J]. *J Am Ceram Soc*, 2022, 105: 606–613.
- [30] ZHANG K, LI W, ZENG J, et al. Preparation of $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ high-entropy transparent ceramic using combustion synthesized nanopowders[J]. *J Alloy Compd*, 2020, 817: 153328.
- [31] MAO A, XIANG H-Z, ZHANG Z-G, et al. Solution combustion synthesis and magnetic property of rock-salt $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ high-entropy oxide nanocrystalline powder[J]. *J Magn Magn Mater*, 2019, 484: 245–252.
- [32] OKEJIRI F, ZHANG Z, LIU J, et al. Room-temperature synthesis of high-entropy perovskite oxide nanoparticle catalysts through ultrasonication-based method[J]. *ChemSusChem*, 2020, 13: 111–115.
- [33] YE F, JIANG X, HUANG X, et al. High sintering activity NaNbO_3 powder synthesis via the polyacrylamide gel method and fabrication of a NaNbO_3 ceramic at lower temperature[J]. *J Mater Res Technol*, 2021, 15: 5833–5840.
- [34] FU M, YANG J, LUO W, et al. Preparation of $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanopowders by polyacrylamide gel method and their sintering behaviors[J]. *J Eur Ceram Soc*, 2022, 42: 1585–1593.
- [35] MOOSAVIFARD S E, EL-KADY M F, RAHMANIFAR M S, et al. Designing 3D highly ordered nanoporous CuO electrodes for high-performance asymmetric supercapacitors[J]. *ACS Appl Mater Inter*, 2015, 7: 4851–4860.
- [36] XU J, SUN Y, LU M, et al. Fabrication of the porous MnCo_2O_4 nanorod arrays on Ni foam as an advanced electrode for asymmetric supercapacitors[J]. *Acta Mater*, 2018, 152: 162–174.
- [37] MNASRI W, BÉRARDAN D, TUSSEAU-NENEZ S, et al. Synthesis of $(\text{MgCoNiCuZn})\text{O}$ entropy-stabilized oxides using solution-based routes: influence of composition on phase stability and functional properties[J]. *J Mater Chem C*, 2021, 9: 15121–15131.
- [38] PHAKATKAR A H, SARAY M T, RASUL M G, et al. Ultrafast synthesis of high entropy oxide nanoparticles by flame spray pyrolysis[J]. *Langmuir*, 2021, 37: 9059–9068.
- [39] QIU N, CHEN H, YANG Z, et al. A high entropy oxide $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$ with superior lithium storage performance[J]. *J Alloy Compd*, 2019, 777: 767–774.
- [40] LIN Y, BIESUZ M, BORTOLOTTI M, et al. Impact of reducing conditions on the stabilization of $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ high-entropy oxide[J]. *Ceram Int*, 2022, 48: 30184–30190.
- [41] NGUYEN T X, PATRA J, CHANG J-K, et al. High entropy spinel oxide nanoparticles for superior lithiation-delithiation performance[J]. *J Mater Chem A*, 2020, 8: 18963–18973.
- [42] TALLURI B, APARNA M L, SREENIVASULU N, et al. High entropy spinel metal oxide $(\text{CoCrFeMnNi})_3\text{O}_4$ nanoparticles as a high-performance supercapacitor electrode material[J]. *J Energy Storage*, 2021, 42: 103004.
- [43] TAN H, ZHAO Z, ZHU W, et al. Oxygen vacancy enhanced photocatalytic activity of perovskite SrTiO_3 [J]. *ACS Appl Mater Inter*, 2014, 6: 19184–19190.
- [44] SILVA T R, SILVA V D, FERREIRA L S, et al. Role of oxygen vacancies on the energy storage performance of battery-type NiO electrodes[J]. *Ceram Int*, 2020, 46: 9233–9239.
- [45] LIANG B, AI Y, WANG Y, et al. Spinel-type $(\text{FeCoCrMnZn})_3\text{O}_4$ high-entropy oxide: Facile preparation and supercapacitor performance[J]. *Materials*, 2020, 13: 5798.
- [46] YANG H, GUO H, LI X, et al. Regulation effects of Co^{2+} on the construction of a $\text{Cu-Ni}(\text{OH})_2/\text{CoO}$ nanoflower cluster heterojunction: a critical factor in obtaining a high-performance battery-type hybrid supercapacitor[J]. *Nanoscale*, 2021, 13: 18182–18191.
- [47] YU F, ZHANG C, WANG F, et al. A zinc bromine “supercapattery” system combining triple functions of capacitive, pseudocapacitive and battery-type charge storage[J]. *Mater Horiz*, 2020, 7: 495–503.
- [48] XU H, CAO Y, LI Y, et al. High-loading Co-doped NiO nanosheets on carbon-welded carbon nanotube framework enabling rapid charge kinetic for enhanced supercapacitor performance[J]. *J Energy Chem*, 2020, 50: 240–247.
- [49] AOKI K J, CHEN J, LIU Y, et al. Peak potential shift of fast cyclic voltammograms owing to capacitance of redox reactions[J]. *J Electroanal Chem*, 2020, 856: 113609.
- [50] LIU G, SONG X-Z, ZHANG S, et al. Hierarchical $\text{CuO}@\text{ZnCo-OH}$ core-shell heterostructure on copper foam as three-dimensional binder-free electrodes for high performance asymmetric supercapacitors[J]. *J Power Sources*, 2020, 465: 228239.