

空心球状高熵钙钛矿氧化物的制备及其超级电容和电催化析氧性能

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摘 要: 采用微波溶剂热和煅烧处理相结合的方法制备了空心球状的高熵钙钛矿 $\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$ 粉体(HS-HEPs), 并研究了其超级电容和电催化析氧(OER)性能。结果表明, HS-HEPs 在 1 A/g 的电流密度下具有 406 F/g 的比电容, 经过 5000 次充放电循环后, 电容保持率为 65%; HS-HEPs//AC(活性炭)非对称超级电容器在 746 W/kg 的功率密度下, 能量密度可达 39.4 W·h/kg。此外, HS-HEPs 在碱性电解液(1 mol/L KOH 溶液)中, 表现出较好的 OER 性能, 在 10 mA/cm²电流密度下的过电位为 347 mV, Tafel 斜率为 54.13 mV/dec, 并具有良好的电化学稳定性。本研究提供了一种制备空心球状高熵氧化物的方法, 并为设计和开发具有优异超级电容及 OER 性能的材料提供了思路。

关键词: 高熵氧化物; 钙钛矿; 空心球状; 超级电容器; 电催化析氧

中图分类号: TB383 文献标志码: A 文章编号: 0454-5648(2025)09-2651-13

网络出版时间: 2025-06-19



1 Introduction

With the ever-increasing demand for clean and sustainable energy, intensive studies are conducted to develop new technologies for energy storage and conversion^[1-3]. In terms of energy storage, supercapacitors have attracted much attention due to their higher power density, longer cycle life and faster charge/discharge rates in batteries. However, the energy density of supercapacitors is relatively low, which is an obstacle to their practical applications^[4-5]. Some studies^[6-9] seek the appropriate electrode materials for high-performance supercapacitors since the electrode material plays a key role in the performance of supercapacitors. With respect to energy conversion, the electrocatalytic water splitting becomes popular because of its eco-friendly character, net-zero carbon emission and sustainable clean energy production^[10-13]. The electrocatalytic water splitting process involves two half-reactions, *i.e.*, oxygen evolution reaction (OER)

and hydrogen evolution reaction (HER). These reactions both ideally occur at 1.23 V against the reversible hydrogen electrode (RHE)^[14]. However, the OER is thermodynamically more difficult due to the complex four-electron redox processes, greatly hindering the realization of efficient water oxidation^[15]. It is thus critical for the electrochemical water splitting to search for efficient OER electrocatalysts.

In the past decade, a wide range of materials have been developed to be used as electrode materials for supercapacitors and OER electrocatalysis, such as carbonaceous materials^[16-17], oxides^[18-20], hydroxides^[21-23], sulphides^[24-26], nitrides^[27-29], phosphides^[30-32], MXene^[33-34], MOF^[35-36] and composites^[37-40]. However, there are still some challenges in developing ideal electrode materials for supercapacitors and OER electrocatalysts. It is thus important for the practical applications of supercapacitors and OER electrocatalysts in industry to develop advanced electrode materials with excellent electrochemical performances through scalable synthesis processes.

收稿日期: 2024-12-03。 修订日期: 2024-12-27。

基金项目: 国家自然科学基金(52472064)。

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Received date: 2024-12-03. Revised date: 2024-12-27.

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High-entropy oxides (HEOs) have attracted recent attention in the field of electrochemistry due to their distinctive structural characteristics and unique properties^[41–45]. The multiple-principal elements in HEOs offer the multiple redox pairs and multiple possible active sites, which can enhance the energy storage capacity and the electrocatalytic performance. Furthermore, the exceptional structural stability of HEOs leads to a long-term cycle stability for supercapacitors and OER electrocatalysts^[43–45]. Guo *et al.*^[42] investigated the electrochemical properties of $\text{La}(\text{CoCrFeMnNiAl}_x)_{1/(5+x)}\text{O}_3$ perovskite as supercapacitor electrodes, and they found that it displayed a specific capacity of 340.3 F/g at a current density of 1 A/g. Li *et al.*^[43] reported that $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ nanopowder with a spinel structure had a specific capacitance of 384 F/g at 1 A/g and a relatively high capacitance retention of 60% after 2000 charge–discharge cycles at 5 A/g. Nguyen *et al.*^[44] developed $\text{La}(\text{CrMnFeCo}_2\text{Ni})\text{O}_3$ electrocatalyst, exhibiting an OER overpotential of 325 mV at 10 mA/cm² and electrochemical stability after tests for 50 h. Kante *et al.*^[45] investigated the electrocatalyst properties of $\text{LaCr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{O}_{3-\delta}$ with a perovskite structure, and they found that the electrocatalyst possessed the surprisingly high OER activity due to a synergistic effect of different transition metal cations. Although a notable progress has been achieved in development of HEO electrodes, their electrochemical properties should be further improved to meet the requirements of high-performance supercapacitors and OER electrocatalysts.

It is known that electrochemical properties of electrode materials have a great structural dependence^[46–48]. The abundant active sites for Faradic redox reactions and short pathways for charge transportation could be constructed through the design of novel HEOs with advanced microstructures, thus improving the electrochemical properties^[49–52]. As advanced microstructures, the hollow structure has a great promise for energy storage and conversion because it can provide more accessible storage sites, more catalytic centers and larger electrode/electrolyte contact area^[53]. Besides, the void space of hollow structure can buffer the destructive volume expansion and alleviate stress/strain produced during

cycling, leading to an improved cycling stability^[54]. In addition, hollow structure can also isolate catalytic species, thus enabling the combination of incompatible catalytic functions and cascade reactions^[55]. It is thus expected that the construction of hollow structure could be an alternative route to significantly promote the electrochemical properties of HEOs electrode materials. However, it is difficult to prepare the HEOs with a hollow structure due to the complexity of the high-entropy system. To our knowledge, little work on the HEOs with hollow structure acted as electrode materials of supercapacitors and OER electrocatalysts has been reported yet.

In this work, a hollow spherical high-entropy perovskite oxide of $\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$ (*i.e.*, HS-HEPs) was prepared by microwave solvothermal process and subsequent calcination treatment. For high-entropy perovskite and special hollow structure, the as-prepared HS-HEPs exhibited excellent electrochemical performance when used as an electrode material for supercapacitors and OER electrocatalysts. This work could provide a strategy to design and prepare hollow spherical high-entropy oxides, having promising applications in energy storage and conversion.

2 Experimental

2.1 Chemicals

Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, AR), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, in mass), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%) (Macklin Chemical Co., Ltd., China) were used without further purifications.

2.2 Preparation of carbon spheres

3 g glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) was dissolved in 50 mL deionized water under stirring for 30 min. The solution was then transferred to a Teflon-coated autoclave (at a filling ratio of 80%) and maintained at 160 °C for 12 h. After cooling to room temperature, the product was centrifuged and washed with deionized water and ethanol for several times. Subsequently, the product was dried in a vacuum drying oven at 70 °C for 12 h to obtain the carbon sphere powder.

2.3 Preparation of HS-HEPs

Fig. 1 shows the preparation process of HS-HEPs.

Typically, 0.134 mmol $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.134 mmol $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.134 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.134 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.134 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 0.5 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 30 mL ethanol under stirring for 1 h to obtain the homogeneous solution. 60 mg of carbon spheres were then added in the solution followed by ultrasonic treatment for 30 min. The resulting mixture was transferred to a 50 mL microwave digestion vessel. Afterwards, the vessel was placed in a microwave oven, and heated at 210 W for 10 min. Subsequently, the obtained mixture was centrifuged, washed with deionized water, and dried in a vacuum drying oven at 70 °C for 12 h. Finally, the obtained precursor powder was calcinated in a tube furnace with a heating rate of 3 °C/min at 650 °C for 2 h to acquire HS-HEPs.

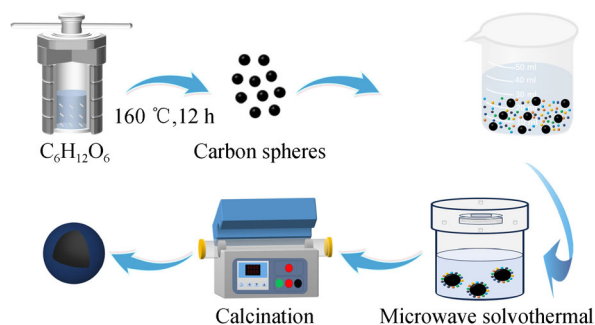


Fig. 1 Schematic illustration of preparation of HS-HEPs

2.4 Characterizations

The crystalline structure of the sample was determined by X-ray diffraction (XRD, D8 Davinci, Bruker Co., Germany). The morphology and microstructure of sample were characterized by field-emission scanning electron microscopy (FESEM, S-4800, Hitachi Co., Japan) equipped with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEOL-2100F, JEOL Co., Japan). The X-ray photoelectron spectra were determined by X-ray photoelectron spectrometry (XPS, ESCALab 250, Thermo VG Co., USA). The heating process of carbon spheres was characterized by differential scanning calorimetry and thermogravimetric analysis (DSC-TGA, Discovery SDT 650, TA Instruments Co., USA) at a heating rate of 10 °C/min in an air atmosphere.

2.5 Electrochemical measurements

The supercapacitor performance of sample was

measured on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China) with a typical three-electrode cell configuration in a 6 mol/L KOH aqueous solution. The working electrode was prepared *via* coating the well-mixed slurry of HS-HEPs, carbon black (Super-P), and polyvinylidene fluoride (PVDF) in a mass ratio of 8 : 1 : 1 on nickel foam (1 cm×1 cm), followed by vacuum drying at 70 °C for overnight. Platinum plate (1 cm×1 cm) was served as a counter electrode, and a saturated calomel electrode (SCE) was used as a reference electrode. For fabricating an asymmetric supercapacitor device, HS-HEPs and activated carbon (AC) were used as a positive electrode and a negative electrode, respectively. NKK-MPF30AC-100 cellulose membrane and 6 mol/L KOH aqueous solution were used as a separator and an electrolyte, respectively.

2.6 Electrochemical measurement of OER

The OER measurements of the samples were also examined by CHI 660E with a three-electrode system in a 1 mol/L KOH aqueous solution. 5 mg of HS-HEPs was added in a mixed solution containing 200 μL of deionized water, 150 μL of anhydrous ethanol, and 40 μL of 5% (in mass fraction) Nafion solution. The resulting mixture was sonicated for 1 h, and then stirred for 1 h to obtain a uniform dispersion. Afterwards, 20 μL of the above well-dispersed suspension was dropped onto nickel foam (1 cm×1 cm) to gain a working electrode. Subsequently, the working electrode was vacuum-dried at 70 °C for overnight. Platinum plate (1 cm×1 cm) was served as a counter electrode, and a saturated calomel electrode (SCE) was used as a reference electrode. The potential was converted to the RHE standard scale by

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.0592 \times \text{pH value} + 0.241 \quad (1)$$

where the pH value of 1 mol/L KOH aqueous solution is 14. Linear sweeping voltammogram (LSV) is performed from 1.1 V to 1.7 V versus RHE at a scan rate of 5 mV/s. Tafel slope is derived from the linear region of the LSV curve.

3 Results and discussion

Fig. 2 shows the DSC-TGA curves of carbon spheres. Clearly, the exotherm from 255 °C to 542 °C accompanied by a great weight loss is due to the

decomposition of the carbon spheres. No weight loss occurs at above 580 °C, implying the completed decomposition of carbon spheres. To completely remove the carbon spheres from the samples, the calcination temperature is 650 °C.

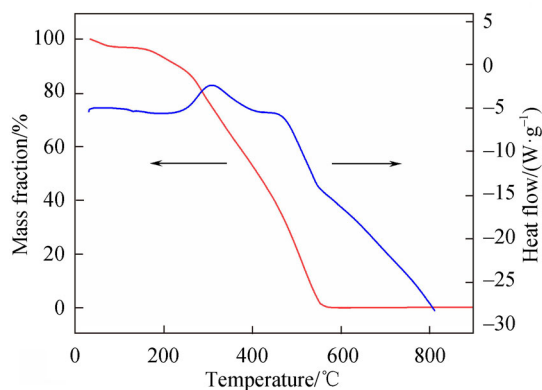


Fig. 2 DSC-TGA curves of carbon spheres

Fig. 3 shows the XRD patterns of HS-HEPs and rietveld refinement, respectively. In Fig. 3(a), the diffraction peaks can be indexed to a cubic perovskite structure, matching well with the perovskite-type LaMnO_3 (JCPDS 75-0440). In Fig. 3(b), the perovskite

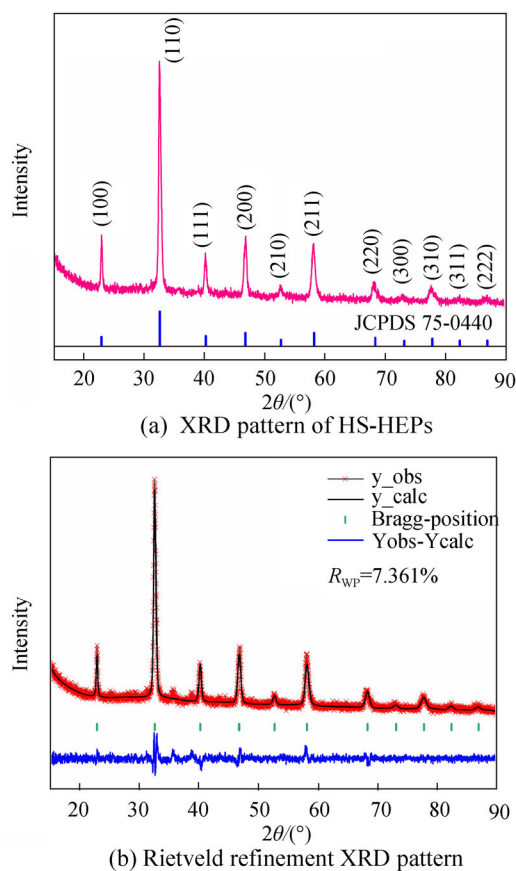


Fig. 3 XRD patterns of HS-HEPs and rietveld refinement

phase of the sample crystallizes in a cubic structure with refined lattice parameters $a=b=c=3.8723 \text{ \AA}$.

Fig. 4 shows the SEM images of carbon spheres, precursors of HS-HEPs, HS-HEPs, and broken HS-HEPs, the HRTEM image of HS-HEPs and SAED pattern. In Fig. 4(a), the well-dispersed spherical carbon particles appear. The diameters of carbon spheres are in the range of 1.3–3.6 μm . In Fig. 4(b), the amorphous precursors are grown *in-situ* on the surface of the carbon spheres after a microwave-assisted solvothermal process. In Figs. 4(c) and 4(d), the carbon spheres are removed after the calcination at 650 °C, thus preparing the samples with a hollow sphere structure. Moreover, the hollow sphere structure with a porous shell structure is formed due to the accumulation of many nanoparticles. This porous hollow structure can provide a great specific surface area for charge storage and a reduced length for both mass and charge transport. In Fig. 4(e), the measured lattice fringe spacing of 0.193 and 0.121 nm corresponds well to planes (200) and (310) of the cubic LaMnO_3 perovskite, respectively. In Fig. 4(f), the diffraction rings can be indexed to planes (110), (111), (200), (210), (211), and (220) of perovskite phase, which can consistent with the XRD patterns. Fig. 5 shows the EDS elemental mapping.

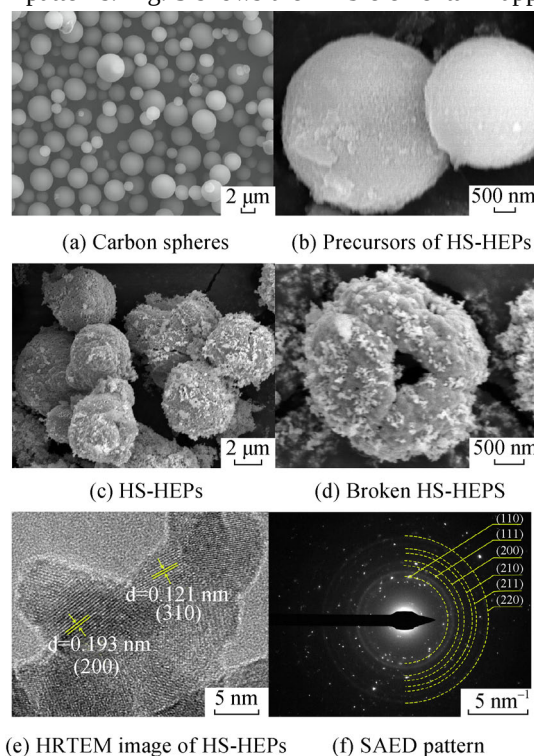


Fig. 4 SEM images of carbon spheres, precursors of HS-HEPs, HS-HEPs, and broken HS-HEPs, HRTEM image of HS-HEPs as well as SAED pattern

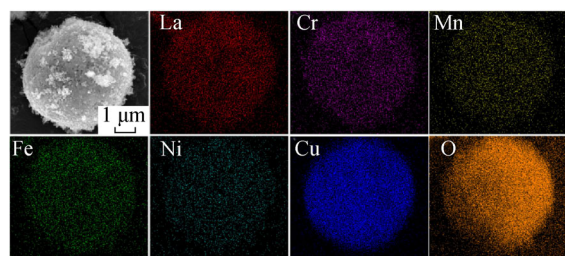


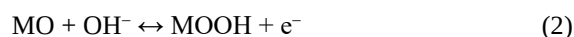
Fig. 5 SEM-EDS mapping of HS-HEPs

Clearly, the elements are uniformly distributed in the entire sample, indicating the compositional uniformity of HS-HEPs.

The valence states of elements in HS-HEPs are studied by XPS. The survey spectrum shown in Fig. 6(a) reveals the presence of La, Cr, Mn, Fe, Ni, Cu, and O elements, along with C element mainly from the adsorbed carbon dioxide. In Fig. 6(b), the high-resolution XPS of La 3d is expressed as La 3d_{3/2} and La 3d_{5/2} due to the Cr³⁺ species^[56]. Fig. 6(c) shows the high-resolution XPS of Cr 2p. Clearly, the Cr 2p_{3/2} spectrum can be deconvoluted into two peaks at 576.6 and 579.8 eV, corresponding to Cr³⁺ and Cr⁶⁺, respectively^[57]. In Fig. 6(d), two peaks at 642.2 eV and 653.9 eV can occur, corresponding to the Mn 2p_{3/2} and Mn 2p_{1/2}, respectively. The Mn 2p_{3/2} peak can be deconvoluted into Mn³⁺ and Mn⁴⁺ at 641.5 eV and 643.5 eV, respectively^[44]. The high-resolution spectrum of Fe 2p (see Fig. 6(e)) shows the two major peaks at 710.9 eV and 723.8 eV, which are attributed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively^[42]. The deconvolution of the Fe 2p_{3/2} peak indicates the coexistence of Fe²⁺ and Fe³⁺^[44]. In the XPS of Ni 2p (see Fig. 6(f)), two fitted peaks located at 851.5 eV and 855.5 eV correspond to Ni²⁺ and Ni³⁺, respectively^[56]. The Cu XPS spectrum (see Fig. 6(g)) represents two satellites in one shakeup orbit and two doublets in spin orbit, including a Cu²⁺ doublet at 934.9 eV and 954.9 eV and a Cu⁺ doublet at 932.8 eV and 952.5 eV. In Fig. 6(h), the high-resolution XPS of O 1s is deconvoluted into three peaks at 530.0, 531.7 eV, and 533.3 eV, corresponding to the lattice oxygen (O_L), oxygen vacancy (O_V), and chemisorbed oxygen (O_C), respectively^[43]. The proportion of O_V is 25.28%, revealing a high oxygen vacancy content in the HS-HEPs. The presence of variable oxidation states of Cr, Fe, and Mn in the HS-HEPs benefits the Faradaic redox reactions, which favors to increase the capacitance^[4]. In

addition, the existence of high concentration of oxygen vacancies is beneficial to enhancing the capacitance and OER activity^[12].

The electrochemical supercapacitive performances of HS-HEPs are studied to verify its application potential in the field of energy storage. The electrochemical properties of HS-HEPs are investigated in 6 mol/L KOH aqueous solution by a standard three-electrode system. Fig. 7(a) shows the cyclic voltammetry (CV) curves at different scan rates in a potential range of 0.0–0.5 V. The symmetric redox peaks can appear in all CV curves, implying the pseudocapacitance characteristics of the electrode materials. Moreover, the peak current increases with the increase of scan rate, indicating the fast electron and ion transport rates^[58]. The possible charge storage mechanism can be described by the following redox reactions:



where M represents the metal elements.

To further distinguish the types of charge storage mechanism of HS-HEPs, the electrochemical kinetic analysis is performed. According to the empirical formula, the peak current (i) and scan rate (v) in CV profile obey the power law^[59]:

$$i = av^b \quad (3)$$

where a and b are adjustable values. When b value approaches to 0.5, the electrochemical reaction is an ideally diffusion-controlled Faraday intercalation process. When b value reaches to 1, the electrochemical behavior is controlled by capacitance. According to the CV curves (see Fig. 7(a)), the plot of $\lg(i)$ versus $\lg(v)$ is obtained and shown in Fig. 7(b). The calculated b values for anodic and cathodic peaks are 0.58 and 0.61, respectively. It can be thus inferred that the charge storage of HS-HEPs is synergistically controlled by capacitive behavior and diffusion behavior, which is favorable for the fast ion diffusion kinetics^[60].

Fig. 7(c) shows the galvanostatic charge-discharge (GCD) curves of HS-HEPs at various current densities ranging from 1 to 20 A/g with a potential window of 0.0–0.5 V. The GCD curves with the voltage plateaus confirm the pseudocapacitance nature of electrode material. Moreover, the GCD curves are symmetric, indicating the high reversibility and superior storage

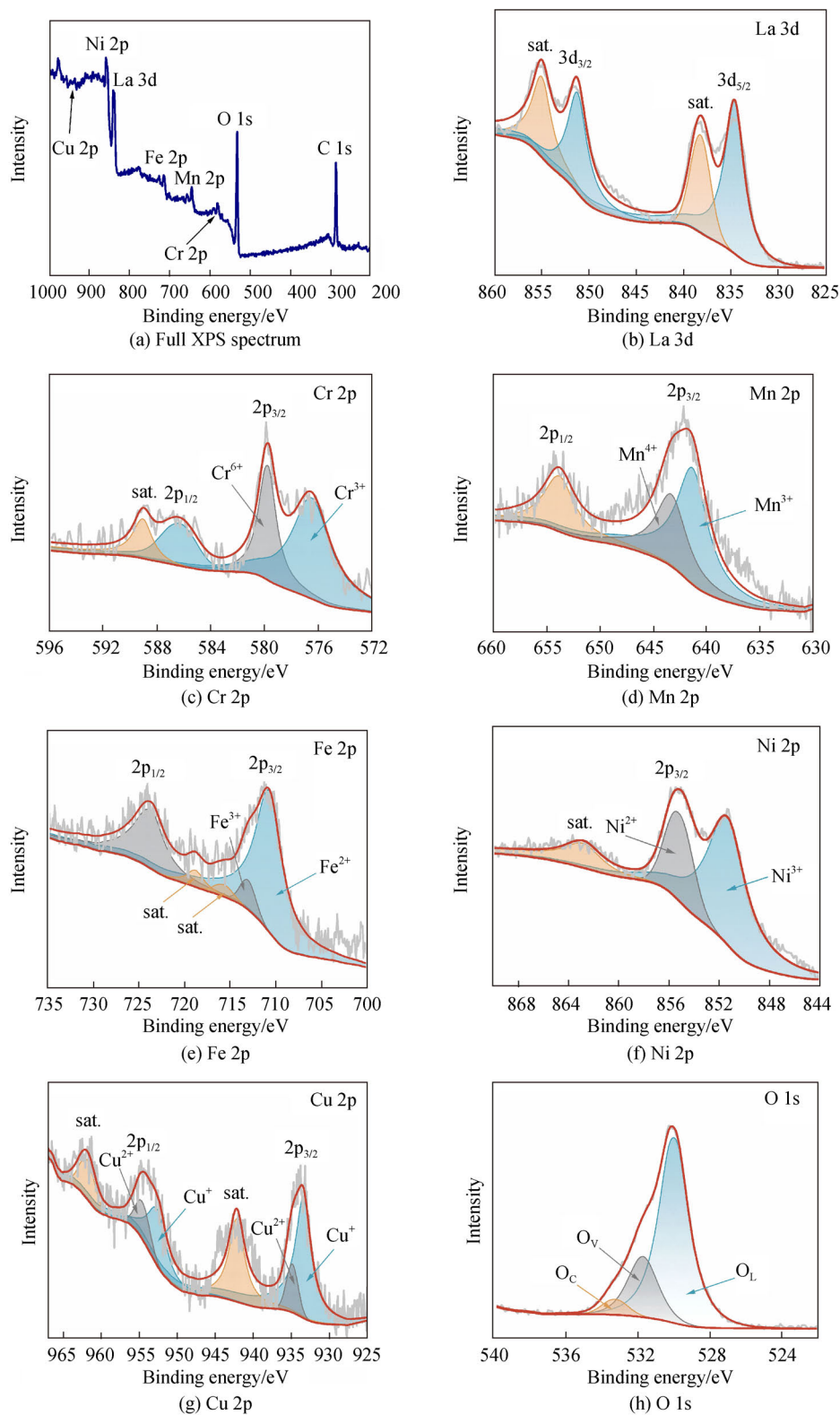


Fig. 6 Full XPS spectra and high-resolution XPS spectra of La 3d, Cr 2p, Mn 2p, Fe 2p, Ni 2p, Cu 2p, and O 1s

efficiency. Based on the GCD curve, the specific capacitance (C_s) of HS-HEPs is estimated by

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (4)$$

where I , Δt , m and ΔV are the discharge current, discharge time, mass of active material, and discharging potential range, respectively. The specific capacitances of HS-HEPs are calculated to be 406, 388, 376, 360, and

334 F/g at 1, 2, 3, 5, 10, and 20 A/g, respectively. A high rate capability with 69% retention at 20 A/g is obtained, as shown in Fig. 7(d). Compared with the other perovskite oxides and high-entropy oxides reported in literature^[39,42,61], HS-HEPs exhibit the high specific capacitance and rate capability, which can be attributed to the synergistic effect of the multi-component metal and

special hollow sphere structure. The cycling performance of HS-HEPs is evaluated by GCD cycles of 5000 at a current density of 5 A/g. In Fig. 7(e), 65% capacitance is retained after 5000 cycles. The HS-HEPs exhibits a good long-term electrochemical stability, which is further proved by the stable charge-discharge curve for the last 15 cycles, as shown in an inset of Fig. 7(e).

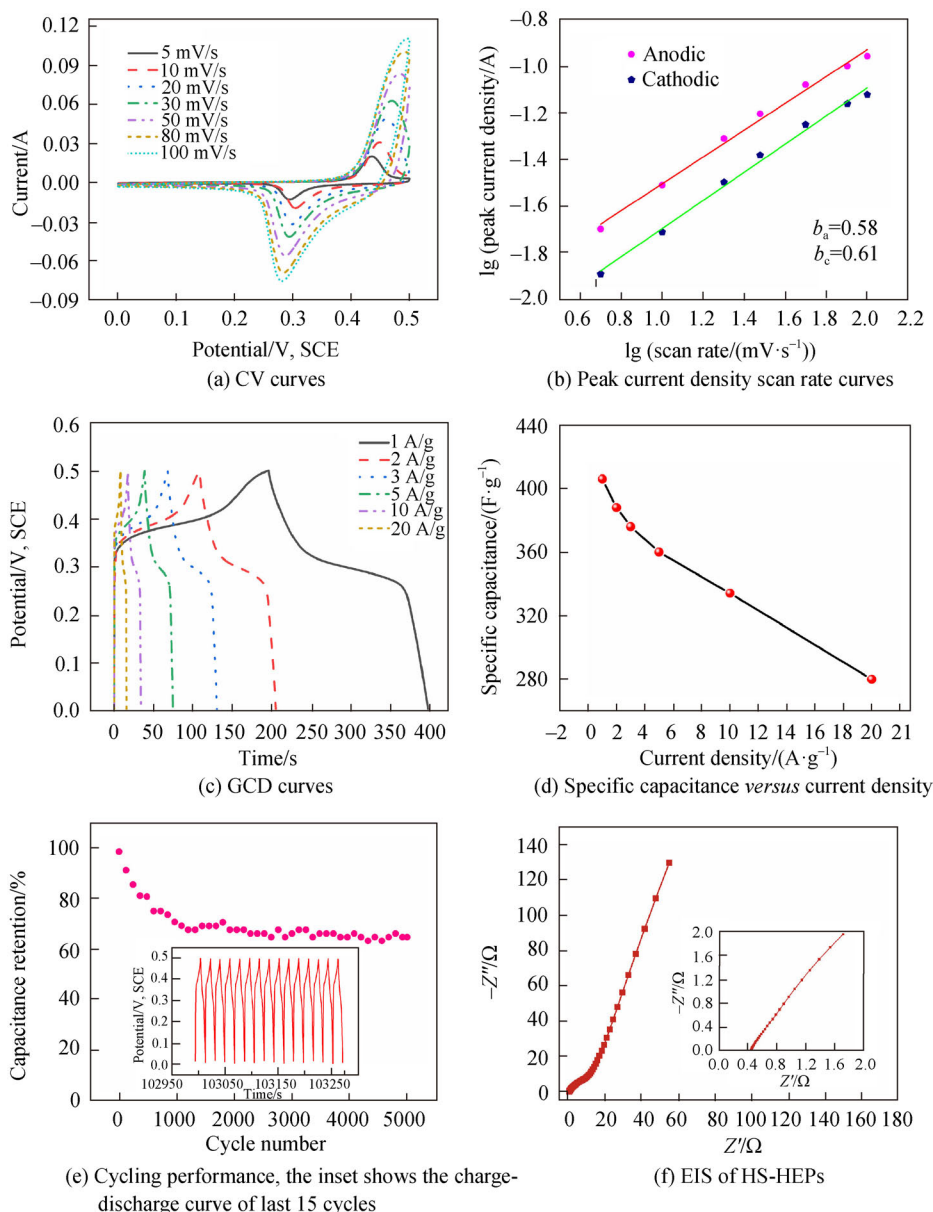


Fig. 7 CV curves (a), peak current density versus scan rate curves (b), GCD curves (c), specific capacitance versus current density (d), cycling performance, the inset shows the charge-discharge curve of the last 15 cycles (e), and EIS of HS-HEPs (f)

Fig. 7(f) shows the Nyquist plot recorded in a frequency range of 0.01–100.00 kHz at an open circuit potential with an amplitude of 5 mV. The slope of the linear plot at a low frequency relates to the Warburg impedance (R_w)^[46]. Therefore, the nearly vertical straight

line reveals a low R_w of HS-HEPs, implying a fast ion diffusion within electrodes. Furthermore, the intersection of the Nyquist plot with the real axis stands for the series resistance (R_s)^[42]. In the inset of Fig. 7(f), HS-HEPs have a low R_s value of 0.45 Ω . Consequently, the low R_w and

R_s result in the good conductivity and rapid ion transport kinetics.

For the practical applications of HS-HEPs, an asymmetric supercapacitor device (HS-HEPs//AC) with a two-electrode configuration is assembled. Fig. 8(a) shows the CV curves of HS-HEPs and AC at a scan rate of 5 mV/s. The potential window of HS-HEPs is in the range of 0.0–0.5 V, while that of AC is in the range of –1.0–0.0 V. The CV curve of AC displays a nearly rectangular shape, revealing a typical electric double-layer capacitor behavior for the negative electrode. Clearly, the working potential window of asymmetric supercapacitor can be expanded to 1.5 V, beyond the thermodynamic

decomposition voltage of water (1.23 V). Fig. 8(b) shows the CV curves of the asymmetric supercapacitors at various scan rates ranging from 5 mV/s to 200 mV/s. The CV curves are a mix of HS-HEPs and AC. The apparent redox peaks in the CV curves demonstrate a pseudocapacitance behavior of asymmetric supercapacitor device. The position of redox peaks shifts to converse direction as the scan rate increases, possibly due to the polarization^[46]. Meanwhile, the peak currents gradually increase. However, the shape of the CV curves at different scan rates is similar, indicating that the asymmetric supercapacitor possesses the good rate capability and reversibility.

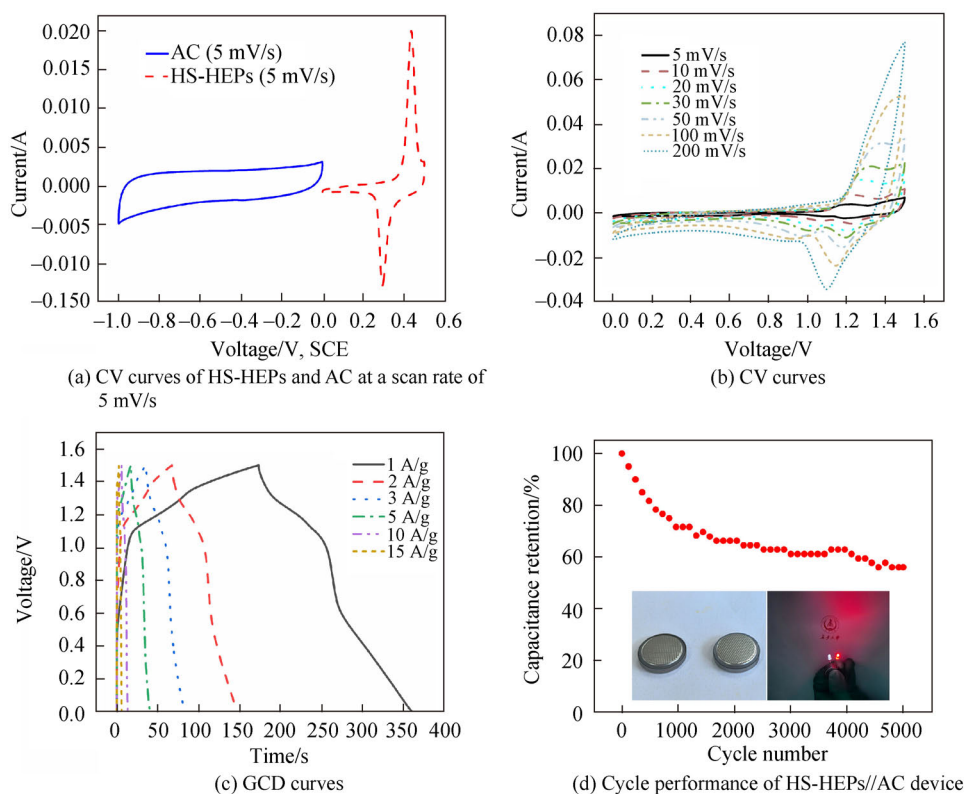


Fig. 8 CV curves of HS-HEPs and AC at a scan rate of 5 mV/s (a), CV curves (b), GCD curves (c), and cycle performance of HS-HEPs//AC device (d), the inset showing that two LED bulbs are illuminated in HS-HEPs//AC device

Fig. 8(c) shows the GCD curves of the asymmetric supercapacitor device at various current densities. The distinct plateau region in GCD curves further reveals the pseudocapacitance behavior of asymmetric supercapacitor device. Moreover, the GCD curves are nearly symmetric, implying a high electrochemical reversibility. According to the GCD curves, the specific capacitances are calculated to be 126, 108, 96, 77, 50 F/g and 33 F/g at

current densities of 1, 2, 3, 5, 10 A/g and 15 A/g, respectively. The energy density E and power density P of the HS-HEPs//AC device are calculated as follows:

$$E = \frac{C_s \Delta V^2}{7.2} \quad (5)$$

$$P = \frac{3600E}{\Delta t} \quad (6)$$

where C_s , ΔV and Δt are the specific capacitance,

voltage window (1.5 V), and discharge time, respectively. A maximum energy density of 39.4 W·h/kg is achieved at a power density of 746 W/kg. Compared with other supercapacitors prepared with high-entropy material, HS-HEPs//AC supercapacitor device shows a high energy density^[62–64]. Furthermore, HS-HEPs//AC device displays a capacitance retention of about 55% after 5000 cycles at 5 A/g, as shown in Fig. 8(d). The practical application of HS-HEPs//AC device is demonstrated in the inset of Fig. 8(d), showing that two LED bulbs are illuminated in HS-HEPs//AC device.

The OER activity of HS-HEPs is evaluated by linear sweep voltammetry (LSV) polarization curve in 1 mol/L KOH aqueous solution using a standard three-electrode system. In Fig. 9(a), the over potential of HS-HEPs is identified as 347 mV *versus* RHE for achieving a current density of 10 mA/cm², which is smaller than that of commercial IrO₂ (372 mV)^[65]. The OER kinetics of the HS-HEPs is further investigated by the Tafel slope. In general, the small value of the Tafel slope indicates the fast kinetics. In Fig. 9(b), the value of the Tafel slope is 54.13 mV/dec, which is smaller than that of commercial IrO₂ (*i.e.*, 60 mV/dec)^[66]. The results indicate that HS-HEPs have the excellent catalytic activity, showing

promising applications in the field of energy conversion. The electrochemical active surface area (ECSA) is essential for the catalytic performance of catalyst, reflecting the number of active sites involved in the OER. The ECSA of HS-HEPs is thus estimated by where A stands for the geometric area of working electrode (*i.e.*, 1 cm²), C_{dl} is the electrochemical double-layer capacitance (C_{dl}), C_s is the specific capacitance of 0.04 mF/cm². The C_{dl} value can be measured through CV curves within the non-Faradaic potential range. In Fig. 9(c), the difference ($\Delta j/2$) between anodic and cathodic current densities at the middle potential is plotted as a function of scan rate, where the slope of the linearly fitted line is determined as the C_{dl} value. The C_{dl} value of HS-HEPs is 5.91 mF/cm². The ECSA of HS-HEPs is hence estimated to be 147.75 cm². The relatively large ECSA is attributed to the enormously accessible active sites on the surface and the porous nature of hollow structure, which facilitate the fast reaction kinetics of HS-HEPs. The long-term stability of electrocatalysts is important for the practical application. Fig. 9(d) shows the chronoamperometry plot of HS-HEPs at a current density of 10 mA/cm² for 50 h. The potential is basically unchanged for 50 h, exhibiting an excellent OER stability.

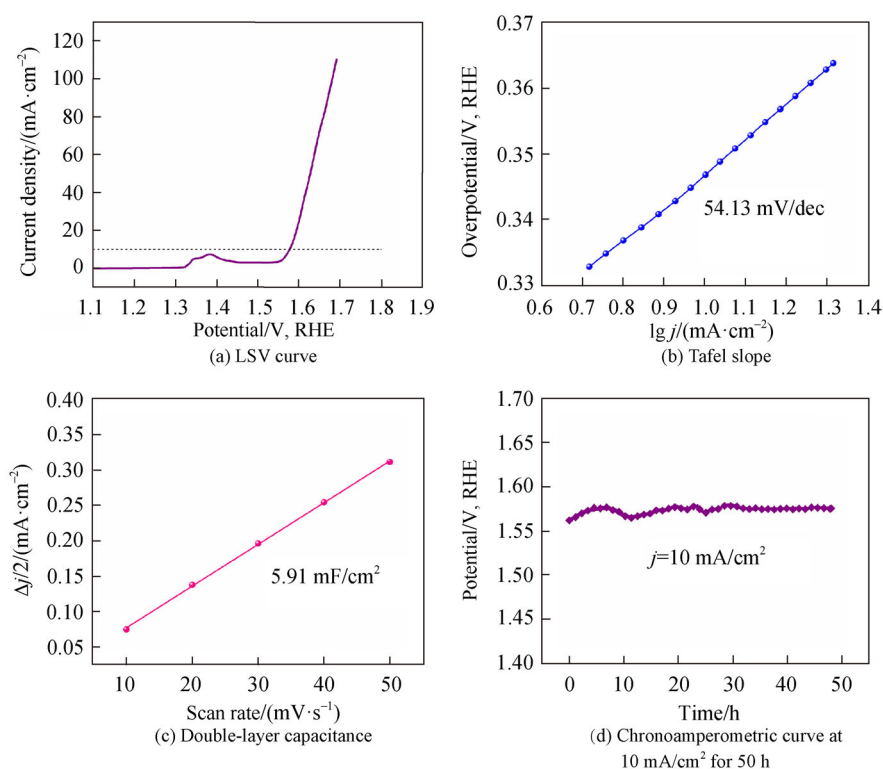


Fig. 9 LSV curve, Tafel slope, double-layer capacitance, and chronoamperometric curve at 10 mA/cm² for 50 h

4 Conclusions

High-entropy $\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$ hollow spheres with a perovskite crystalline structure were prepared by microwave solvothermal process and subsequent calcination treatment. The HS-HEPs possessed the excellent electrochemical performance, which could be ascribed to the high specific surface area, abundant active sites, and high oxygen vacancy content, resulting from the combination of high-entropy perovskite and special hollow structure. According to the electrochemical performance, HS-HEPs could be used as a supercapacitor electrode material and OER electrocatalysts. This work could provide a strategy to design and prepare high-entropy oxides with a hollow sphere structure, thus having promising applications in energy storage and conversion.

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Hollow Spherical High-Entropy Perovskite Oxide for Supercapacitor and OER Applications

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Extended Abstract

Introduction High-entropy oxides (HEOs) have attracted much attention in the field of electrochemistry due to their distinctive structural characteristics and unique properties. The multiple-principal elements in HEOs offer the multiple redox pairs and multiple possible active sites, which can enhance the energy storage capacity and the electrocatalytic performance. Although the notable progress is achieved in the development of HEOs electrodes, their electrochemical properties should be further improved to meet the requirements of high-performance supercapacitors and OER electrocatalysts. The abundant active sites for the Faradic redox reactions and short pathways for charge transportation could be constructed through the design of novel HEOs with advanced microstructures, thus improving the electrochemical properties. As advanced microstructures, a hollow structure has a great promise for energy storage and conversion because it can provide more accessible storage sites, more catalytic centers and a larger electrode/electrolyte contact area. It is thus expected that the construction of hollow structure is an alternative route to significantly promote the electrochemical properties of HEOs electrode materials. However, it is difficult to prepare the HEOs with a hollow structure due to the complexity of the high-entropy system.

In this work, a hollow spherical high-entropy perovskite oxide of $\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$ (HS-HEPs) was prepared by microwave solvothermal process and subsequent calcination treatment. The as-prepared HS-HEPs exhibited the excellent electrochemical performance when used as an electrode material for supercapacitors and OER electrocatalysts due to the advantages resulted from the combination of high-entropy perovskite and special hollow structure.

Methods HS-HEPs were prepared by microwave solvothermal process and subsequent calcination treatment. Typically, 0.134 mmol $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.134 mmol $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.134 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.134 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.134 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 0.5 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 30 mL ethanol under stirring for 1 h to obtain the homogeneous solution. Afterwards, 60 mg of carbon spheres were added in the solution under ultrasonic treatment for 30 min. The resulting mixture was transferred to a 50 mL microwave digestion vessel. The vessel was heated in a microwave oven at a power of 210 W for 10 min. Subsequently, the obtained mixture was centrifuged, washed with deionized water, and dried in a vacuum drying oven at 70 °C for 12 h. Finally, the obtained precursor powder was calcinated in a tube furnace with a heating rate of 3 °C/min at 650 °C for 2 h to acquire HS-HEPs.

The crystalline structure of the sample was determined by X-ray diffraction (XRD, D8 Davinci, Bruker Co., Germany). The morphology and microstructure of sample were characterized by field-emission scanning electron microscopy (FESEM, S-4800, Hitachi Co. Ltd., Japan) equipped with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, 2100F, JEOL Co., Japan). The X-ray photoelectron spectra were obtained by a X-ray photoelectron spectrometry (XPS, ESCALab 250, Thermo VG Co., USA). The supercapacitor and OER performance of the sample were measured on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China).

Results and discussion The as-prepared samples display a cubic perovskite crystalline structure and a hollow sphere morphology. According to the XPS analysis, the variable oxidation states of Cr, Fe and Mn present in the HS-HEPs, which benefits the Faradaic redox reactions and increases the capacitance. In addition, the existence of high concentration of oxygen vacancies in HS-HEPs is beneficial to enhancing the capacitance and OER activity. Based on the GCD curve, the specific capacitance of HS-HEPs is estimated to be 406 F/g at 1 A/g. After GCD cycles of 5000 at a current density of 5 A/g, 65% capacitance is retained, implying a good long-term electrochemical stability. An asymmetric supercapacitor device (HS-HEPs//AC) with a two electrode configuration is assembled. A maximum energy density of 39.4 W·h/kg is achieved at power density of 746 W/kg. The OER activity of HS-HEPs is evaluated by a linear sweep voltammetry (LSV) polarization curve in 1 mol/L KOH aqueous solution using a standard three-electrode system. The overpotential of HS-HEPs is identified as 347 mV versus RHE for achieving a current density of 10 mA/cm², which is

smaller than that of commercial IrO_2 (372 mV). The HS-HEPs possess the excellent electrochemical performance, which can be ascribed to the high specific surface area, abundant active sites, and high oxygen vacancy content, resulting from the combination of high-entropy perovskite and special hollow structure.

Conclusions High-entropy $\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_3$ hollow spheres with a perovskite crystalline structure were prepared by microwave solvothermal process and subsequent calcination treatment. The HS-HEPs possessed the excellent electrochemical performance, which could be ascribed to the high specific surface area, abundant active sites, and high oxygen vacancy content, resulting from the combination of high-entropy perovskite and special hollow structure. Based on the electrochemical performance, HS-HEPs could be used as supercapacitor electrode material and OER electrocatalysts. This work could provide a strategy to design and prepare high-entropy oxides with a hollow sphere structure, having promising applications in energy storage and conversion.

Keywords high-entropy oxides; perovskite; hollow spheres; supercapacitors; oxygen evolution reaction