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Fast fabrication of high entropy oxides electrodes for flexible zinc-ion batteries with high electrochemical performance

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Abstract. The expanding world population, increasing energy demand, and looming climate change urge the development of a sustainable energy future while safeguarding our vulnerable environment. To build a new flexible battery system, high entropy oxides are used as electrodes based on zinc-ion batteries. The battery system with the best electrochemical performance can be determined by a series of experimental designs. Here in I propose to develop a HEO electrode using a fast and clean laser deposition method. A series of tests are designed to verify the degree of performance improvement. In the further research planning, the electrode material can be produced with a metal removed from the HEOs alone and using the same synthetic method and performance measurements to determine the roles of each metal in the HEOs. Additionally, the anions in the HEOs can also be varied to study the impact of various anions on the cell's electrochemical performance. Finally, the particle size of the HEOs can be varied to establish a correspondence between particle size and electrochemical performance to facilitate the selection of the optimum particle sizes. The experimental results can further provide a theoretical basis for the commercial application of zinc-ion batteries in flexible power systems.

Keywords: zinc-ion batteries, high entropy oxides, electrochemical performance, high energy and power density.

1. Introduction

Due to the expanding world population, increasing energy demand, and looming climate change, it is crucial that a sustainable energy future is developed while safeguarding our vulnerable environment. For our technologically advanced society, the need for electrochemical energy storage is growing, and new energy storage systems are in the focus of research. Batteries and supercapacitors are emerging research frontiers for future energy storage technology because of the fast charging kinetic, low cost of maintaining, high energy density as well as flexible and simple installation.

Researchers are paying an increasing attention to the creation of flexible wearable energy storage devices as the market share of wearable electronics grows. Flexible power systems with high performance, small size, and superior mechanical stability are highly desired by industry. Although lithium-ion batteries are presently commercially available and offering excellent energy densities and service lives. However, they have issues with a storage of lithium supplies, high costs, and inadequate safety features that prevent them from further development [1]. Compared to lithium-ion batteries, zinc batteries have the advantages of a larger theoretical capacity (820 mAh/g), a lower reaction potential in aqueous solutions (vs 0.76 V for standard hydrogen electrodes) and a two-electron transfer electrode

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reaction [2]. Therefore, flexible zinc-ion batteries are considered as one of the most important lithium-ion battery substitutes in wearable devices. In recent years, researchers have developed flexible zinc-ion batteries (ZIB) and carried out more theoretical studies and specimen preparation [3-5].

1.1. Zinc-ion batteries

A Zn^{2+}-salt electrolyte, a Zn^{2+} storage cathode, and a metallic Zn anode are the main components of a rechargeable ZIB, as seen in Figure 1. When being discharged or recharged, the reversible Zn^{2+} intercalation/deintercalation (cathode) and Zn plating/stripping (anode) mechanisms operate [6]. During discharge, the zinc anode loses electrons to the external circuits and released Zn^{2+} in the electrolyte. Zn^{2+} is transported along an electrochemical potential gradient towards the cathode and eventually becomes a component of the cathode materials' structure. The type and structure of the electrode material as well as the surface characteristics have a significant impact on how effectively the electrochemical processes perform in the cell system. A robust crystal structure of the cathode material with high capacity and ionic conductivity is required for ZIBs in order to provide quick, stable embedding of Zn^{2+}. In terms of microstructure, it should have sufficient porosity to allow for electrolyte penetration for maximum charge transfer efficiency [7].

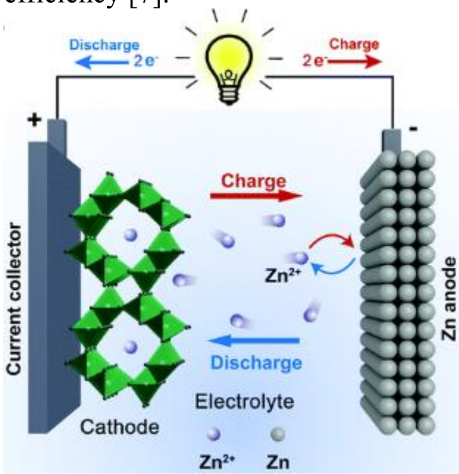

Figure 1. Schematic representation of how rechargeable zinc-ion batteries work [6].

1.2. High entropy oxides

The study of high entropy materials (HEMs) is becoming increasingly popular because of their novel, frequently surprising, and rarely seen features in a variety of applications. High entropy oxides, with exceptional thermal, magnetic, electrical properties and corrosion resistance capabilities, are single-phase, structurally stable solid solutions made from five or more oxides in equal molar ratios. Different metal elements with different radii can occupy the same atomic locations in high entropy oxide (HEO), which can increase the stability of the solid solution's crystal structure. Firstly, the lattice distortion effect can significantly lessen the resistance to ion migration inside the HEO crystal structure when lithium ions are inserted and extracted [8]. Additionally, the production of HEO using a range of elements with various valence states might result in oxygen vacancies, increasing its electrical conductivity [9]. Wang et al. [10] prepared a HEO compound of rock-salt structure that is both multi-anionic and multi-cationic (HEOX) using a transition-metal-based multi-cationic HEO with additional halide (X) and alkali metal ions' assistance. Monovalent lithium (or sodium) is absorbed into the cation lattice of HEO in order to charge-compensate the entry of monovalent fluorine into the anion lattice of HEO, which is formerly occupied by divalent oxygen. Due to the identical ionic radii of fluorine and oxygen (1.33 vs. 1.40, respectively), the single-phase rock-salt structure can withstand replacement without being strained.

Here in I propose to develop a HEO electrode using a fast and clean laser deposition method. The method could be done within a few minutes and free of organic solvents. The as-synthesized nanostructures could feature small and homogeneous particles size, enabling the maximal contact area with the electrolyte. Therefore the batteries based on the prepared electrode would promise fast rate

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capability and high power density combing with low electrical resistance and fast ion diffusion in the high entropy structures. The study will shed light on a facile and inexpensive process of producing a novel flexible zinc-ion battery. HEOs are used as electrodes to enhance the electrochemical performance of the battery. A series of tests are designed to verify the degree of performance improvement. In the further research planning, the electrode material can be produced with a metal removed from the HEOs alone and using the same synthetic method and performance measurements to determine the roles of each metal in the HEOs. Additionally, the anions in the HEOs can also be varied to study the impact of various anions on the cell's electrochemical performance. Finally, the particle size of the HEOs can be varied to establish a correspondence between particle size and electrochemical performance to facilitate the selection of the optimum particle sizes.

2. Experiments

2.1. Synthesis of HEO
HEO is produced using a general and broad methodology, laser scanning ablation (LSA) [11]. At atmospheric pressure and temperature, the appropriate nanoparticles (NPs) precursors are ablated by the LSA approach in alkanes under 5 nanoseconds per pulse. In ethanol, different chloride salts are combined with 0.025 M each metallic element (Co, Cr, Fe, Mn, Ni, Zn), as well as 0.01 M PVP. With a loading of ~1 ml/cm^2, the combined solution is dropped directly onto the carbon cloth. The soaked substrates are subsequently moved to a vacuum oven for room-temperature drying. The substrates are then moved in preparation for laser irradiation. The powder is collected and kept in an environment of ambient temperature.

2.2. Characterization
The morphology of the produced samples is examined using field emission scanning electron microscopy (FE-SEM) as well as transmission electron microscopy (TEM). The element distribution of HEOs is recorded using an EDS equipped TEM. A powder X-ray diffractometer (XRD) is used to measure the crystal structures of the materials using Cu-K radiation (= 1.54178, 40 kV, 40 mA). The samples are digested in aqua regia to create the solutions, which are then diluted with 2% hydrochloric acid. The surface chemistry of HEOs is studied using X-ray photo electron spectroscopy (XPS). Inductively coupled plasma-mass spectrometry (ICP-MS) is used to determine the atomic compositions of the HEOs.

2.3. Electrochemical measurement
The resulting carbon cloth is cut into 1 cm diameter disks and used as half-cell. Electrodeposition on carbon paper is also used to prepare Zn electrode. The electrolyte is made by dissolving 12.5 g $NaSO_4$, 2 g H_3BO_3, and 12.5g $ZnSO_4 \cdot 7H_2O$ in 100mL distilled water. The half-cells are then put together in the glovebox filled with argon, which has an H_2O and O_2 concentration of less than 0.1×10^{-6} each. By using a two-electrode system with a Zn foil counter electrode, the electrochemical performance of HEOs and MnO_2 is assessed. Before the suspension is totally frozen, 4.4 mL of the 0.5 wt% CNF suspension are sequentially poured into the molds. After that, a 36-hour freeze-drying process is performed on the resulting ice monolith to create an integrated aerogel. The polytetrafluoroethylene (PTFE) sheet on which the integrated aerogel is deposited is squeezed to a thin film at a pressure of 5 MPa. The thin film is then dried at room temperature after being reduced by hydrazine vapor for three hours at 100 °C. A piece of separator is sandwiched between the Zn anode and the HEOs cathode to create the Zn/HEOs device. A thin plastic covering is then placed around the integrated gadget. The flexible Zn/HEOs batteries are eventually achieved.

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3. Research Planning

3.1. Verifying Zn/HEOs battery performance

The performance of the galvanostatic discharge/charge (GCD) is evaluated across the potential range of 0.01-3.00 V (vs. Zn^{2+}/Zn). To determine the electrode capacity, the batteries are tested at 0.1 mA/g. The rate performance is measured via GCD at a series of current densities (0.1 mA/g, 0.2 mA/g, 0.5 mA/g, 1 mA/g, 1.5 mA/g, 2 mA/g, 5 mA/g, 10 mA/g). The cycling stability of the device is tested using GCD at 0.1 mA/g for 1000 cycles. The cycling life is defined as the cycle number where the battery reach the 80% of its initial capacity. On the same test equipment, the electrochemical performance of the whole cells is investigated across the voltage range of 0.5 to 4.0 V. On an electrochemical workstation (CHI1000C), cyclic voltammetry (CV) measurements are conducted at various scan speeds ranging from 5 mV/s to 1 V/s in a voltage range of 0.01-3.00 V (vs. Zn^{2+}/Zn). The frequency range used for the electrochemical impedance spectroscopy (EIS) measurements is 10Hz to 1MHz. An voltage of 10 mV is set up for the EIS measurements. Compared with the battery using MnO_2 electrodes, the performance improvement of Zn/HEOs battery is verified by these methods.

The following equation (1) can be used to compute the specific capacity (Cm, mA h g^{-1}) from GCD curves.

$$C_m = (I\Delta t)/m \tag{1}$$

where m is the mass loading, t is the discharging time, and I is the current density.

Following equations (2) (3) can be used to derive mass specific power density P and mass energy density.

$$E = C_m \times \Delta V \tag{2}$$

$$P = (C_m \times \Delta V)/(1000 \times \Delta t) \tag{3}$$

where V is the voltage window.

3.2. The role of the individual elements in HEO electrodes

The performance of the galvanostatic discharge/charge (GCD) is evaluated across the potential range of 0.01-3.00 V (vs. Zn^{2+}/Zn). The performance of the galvanostatic discharge/charge (GCD) is evaluated across the potential range of 0.01-3.00 V (vs. Zn^{2+}/Zn). The multiple transition metals enable a variety of chemical activities towards energy storage. To dissect the role of each element and prove that the current composition offers best performance, I plan to use the same processing to create electrodes that consist of five element compositions and test the performance of each constituent cell with the experimental methods of the first planning. The capacity, rate performance and impedance performance of the different compositions would illustrate the functions of each compositional metal element compared with the six-element electrode.

3.3. Changing the anion of HEO

By tuning the deposition solutions, other high entropy ceramics may be synthesized such as high entropy borides (HEBs), phosphides (HEPs) and nitrides (HENs). To synthesize these materials, the substrates loaded with salt precursors can be submerged in 0.1 M solutions of sodium borohydride, phosphoric acid, and ammonium chloride, respectively prior to laser irradiation. The effects of different anions in ZIBs can be investigated by a continuous EIS test of Zn/HEMs/Zn in addition to the first planned test methods. The anions can tune the electronic structure of cations. Thus, a change in redox activities, thermodynamically voltage window stable are expected.

3.4. Tuning the size of nanoparticles

Particle size and its distribution of nanoparticles play crucial roles in the capacity, charging efficiency and resistance of the batteries. By tuning the amount of capping reagent, polyvinylpyrrolidone (PVP), a tunable metal oxide particle size may be realized. In the synthesis of nanostructured metal oxide materials, PVP also acts as a stabilizer to prevent particle aggregation, but it can also be used to dynamically control the growth of specific facets by combining with other materials. The concentration of PVP can also affect the morphology of the particles [12]. The various size of electrode particles sizes leads to a number of new active sites to the electrolyte and change the reaction rates. The zinc ion exchange is faster at a higher interfacial area. This gives rise to a faster charging of the battery. In general, narrower distributions with smaller particles can lead to better cell performance. However, reducing the particle size has limitations as very small particles exhibit negative effects [13, 14]. Therefore, the connection between electrochemical performance and particle size can be determined experimentally and the particle size corresponding to the optimal battery performance can be obtained.

4. Conclusion

Taking into account population growth, energy shortage and climate change, a new flexible battery system has been built to meet the needs of sustainable development. In the new battery system, high entropy oxide is considered as the electrode of zinc-ion battery. And through a series of experimental design to determine the best electrochemical performance of the battery system. At the same time, a fast and clean laser deposition method for the preparation of HEO electrodes is proposed. In the further research planning, the electrode material can be produced with a metal removed from the HEOs alone and using the same synthetic method and performance measurements to determine the roles of each metal in the HEOs. Additionally, the anions in the HEOs can also be varied to study the impact of various anions on the cell's electrochemical performance. Finally, the particle size of the HEOs can be varied to establish a correspondence between particle size and electrochemical performance to facilitate the selection of the optimum particle sizes. The experimental results can further provide a theoretical basis for the commercial application of zinc-ion batteries in flexible power systems.

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