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The Anode Performance of the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ High Entropy Oxide for Li-Ion Batteries

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Abstract: High-entropy oxides (HEOs), which are new class of single-phase solid solution materials, have recently attracted as electrode material due to their Li-ion storage properties. In this work $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ high entropy oxide was synthesized by conventional solid state method to evaluate its electrochemical performances as anode in the Li-ion battery. The structure of the synthesized $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ was characterized by using X-ray diffraction and field emission - scanning electron microscope techniques. The synthesized high entropy oxide was observed to have single phase rock salt crystal structure. The electrochemical performance of the anode was evaluated by assembling CR2016 type coin cell. Galvanostatic charge/discharge tests showed that the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ anode delivers a high initial discharge capacity of 1668 mA h g^{-1} at a current of 200 mAg^{-1}. The capacity cyclic stability was observed as also satisfactory. These performance values show that the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ high entropy oxide has good potential to be used as anode in Li-ion batteries.

Keywords: Conversion type anode, Li-ion battery, High entropy oxide

Introduction

Li-ion batteries (LIBs) with high cycling stability and reversible capacity are promising energy storage devices to meet the rapid development of electric vehicles. Transition metal oxides have been intensely studied over the past decades as anode material for LIBs due to their high reversible capacity and low cost properties (Kim et al., 2019; Puthusseri et al., 2018). Investigations on the transition metal oxide anodes focus mainly on adjusting the structural properties such as morphology, size, and defect formation in order to solve their fundamental problems which are low Coulombic efficiency (CE), unstable solid electrolyte interface (SEI) film formation, large potential hysteresis, and poor cycling and rate capability (Yuan et al., 2014; Lu et al., 2018; Yu et al.,2018).

Firstly, it is reported by Sarkar et al, the entropy stabilization results in improved cycling capability in (MgCoNiCuZn)O anode (2018). Furthermore, the specific capacity value of 920 mA h g^{-1} was reached after 300 cycles upon synthesis of HEO based anode in the form of nanoparticles (Qiu et al., 2019). Moreover, the (MgCoNiCuZn)O HEO anode with the NCM111 cathode provided 300 mA h g^{-1} full cell capacity after 50 cycles (Wang et al., 2019). In another study, $(MgCoNiZn)_{1-x}Li_xO$ HEOs were synthesized and their electrochemical performances were investigated as anode material in LIBs. The increase in the lithium cation concentration causes generation of more oxygen vacancies, which greatly affected the electrochemical performance of $(MgCoNiZn)_{1-x}Li_xO$ HEO based anodes, on the structure. They reported the $(MgCoNiZn)_{0.65}Li_{0.35}O$ anode had 1930 mA h g^{-1} initial and 610 mA h g^{-1} stable discharge capacities (Lökçü et al., 2020). These results were very promising for the use of HEOs as anode material in LIBs. Besides the (MgCoNiCuZn)O rock-salt type HEO anode, spinel type $(Mg_{0.}2Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})_3O_4$ and $(FeCoNiCrMn)_3O_4$

HEO anodes were synthesized and their electrochemical performances were investigated in LIBs (Wang et al., 2020; Chen et al., 2020). Herein, we synthesized the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ high entropy oxide to further investigation the effect of entropy stabilization on the electrochemical properties of HEO based anodes.

Materials & Methods

MgO, CoO, NiO, ZnO, Li_2O and CuO were mixed homogeneously in the determined molar ratios to get $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ stoichiometry and they milled at 300 rpm for 2 h by using the planetary ball mill (Fritsch Pulverisette 7 Premium Line). The obtained oxide mixture was then unaxially pressed at 300 MPa. Finally, the oxide pellet was sintered at 1000ºC for 12 h prior to the air quenching. The sintered pellet was re-milled at 200 rpm for 1 h to prepare electrodes.

The phase structure of the as-synthesized $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ was examined by XRD (PANalytical Empyrean) and FE-SEM techniques using Cu Kα radiation ($\lambda = 0.154$ nm). The HEO based anode was prepared by mixing 75 wt% active material, 15 wt% carbon black (Super P) and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone (NMP) to form a homogeneous slurry. Then the slurry was coated onto Cu foil and dried in a vacuum oven at 80ºC for 12 h.

The coin cell was assembled in an argon-filled glove box with H_2O and O_2 levels less than 1.0 ppm. Lithium metal was used as the counter and reference electrodes and the glass microfiber filter as a separator. 1 M Lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate and dimethyl carbonate (EC:DMC) in a 1:1 ratio by volume was used as electrolyte. The charge-discharge tests were performed galvanostatically in a potential range change between 0.01 V and 3.00 V (vs. Li^+/Li) at 200 mA g^{-1} current density.

Results and Discussion

The XRD pattern of $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$, which is prepared by the conventional solid state method is given in Figure 1. The $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ shows a typical face-centered-cubic (FCC) rock-salt type structure. Figure 2 shows the FE-SEM images of the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ particles, which is re-milled at 200 rpm for 1 h. As shown in Figure 2, there is no secondary phases and the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ sample was successfully synthesized. Moreover, the size of particles in the range of 300-400 nm can be seen in Figure 2.

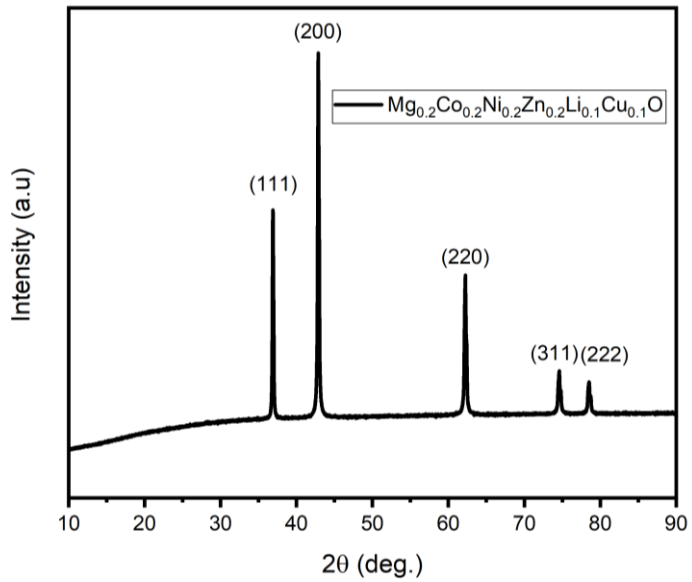

Figure 1. XRD pattern of the as-synthesized $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$.

In order to determine electrochemical properties of the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ anode, galvanostatic charge/discharge tests were performed between 0.01 and 3.0 V vs. Li/Li^+ (Figure 3). The initial discharge capacity of $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ anode is 1668 mA h g^{-1}. The open circuit voltage (OCV) of the fabricated coin-cell is ~2.60 V and the discharge plateau of anode is around 0.75 V for the first cycle process.

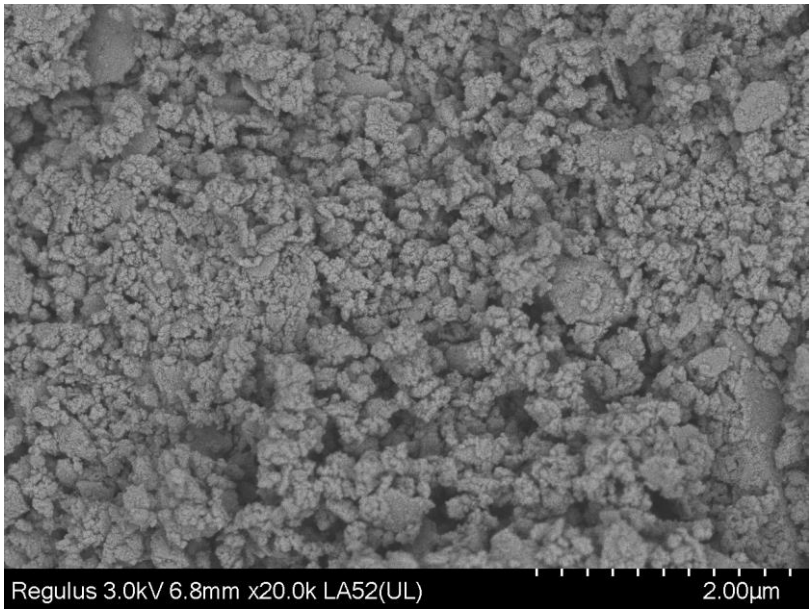

Figure 2. FE-SEM image of the as-synthesized $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$.

The following charge-discharge cycles also are given in Figure 3. The discharge voltages of the anodes look slightly increased and the discharge reaction occurs over a potential range of ~1.60-0.01 V with an inclined single slope. After the first cycle, the significant capacity loss is observed because of the formation of the SEI layer at the interface of the electrode surface and the electrolyte and initial lithium loss, mainly due to anode conversion (Lökçü et al., 2020). The discharge capacity of the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ anode is 724 mA h g^{-1} at the end of 5^{th} cycle.

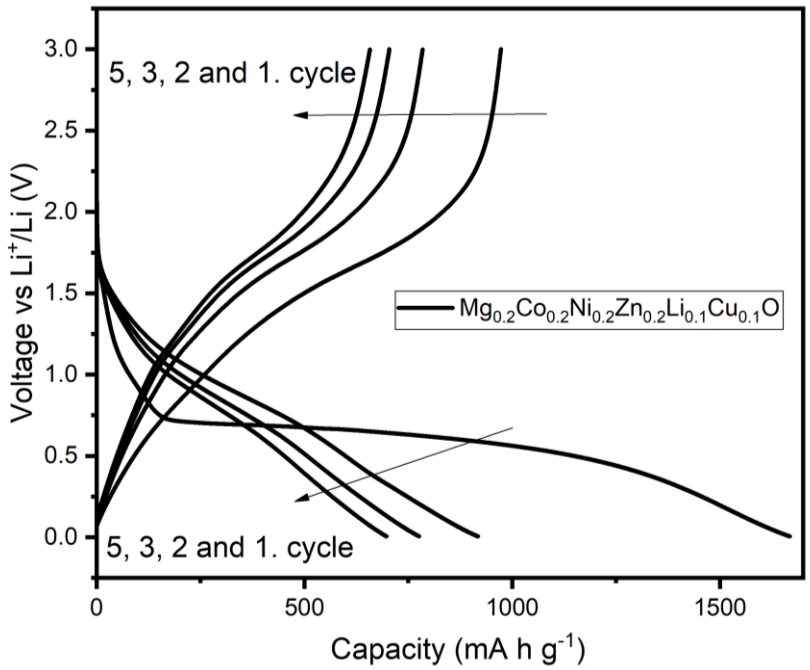

Figure 3. Charge/discharge curves of $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ anode at a current density of 200 mA g^{-1}.

The CV curve of the synthesized $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ for two cycles is given in Figure 4. In the first cycle, sharp peak appears at 0.25 V in the cathodic scan, corresponding to the processes of initial reduction of transition metal oxides and the formations of both Li_2O and the SEI layer (Lökçü et al., 2020). In the second cycle, ths sharp peaks transforms into wider peaks and it shifts to the more positive potentials. This phenomenon, which indicates the irreversibility of the initial lithiation process and the SEI formation, is commonly observed in the conversion-type anode materials (Lökçü et al., 2020; Chen et al., 2020).

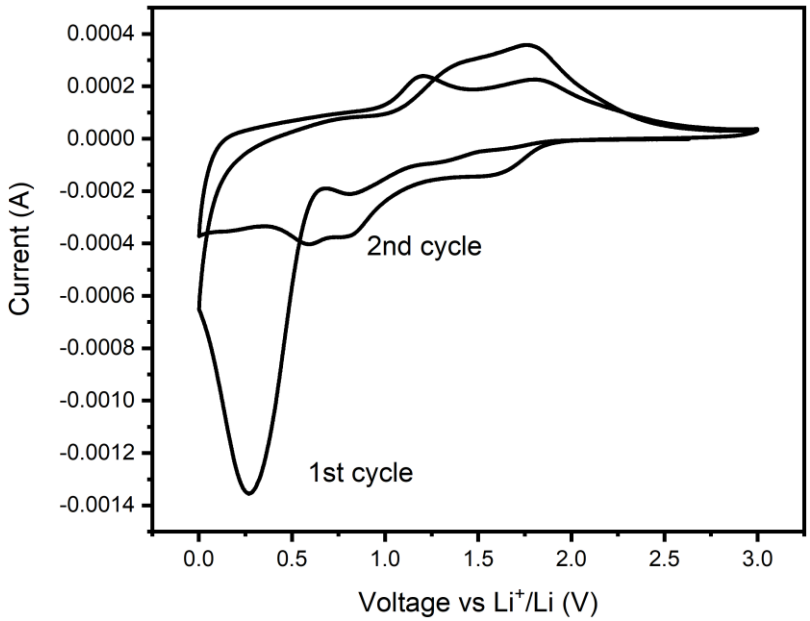

Figure 4. CV curve of a $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ anode vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1} during the first 2 cycles.

Conclusion

In this work, we synthesized the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ high entropy oxide and investigated its electrochemical properties in LIB as an anode material. Charge/discharge measurements showed that the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ anode delivers a high initial discharge capacity of 1668 mA h g^{-1} at a current of 200 mAg^{-1}. Moreover, the capacity cyclic stability was observed as also satisfactory. These results prove that the $Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.1}Cu_{0.1}O$ high entropy oxide has good potential to be used as conversion-type anode in Li-ion batteries.

Acknowledgements or Notes

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