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Effect of Co Content on the Electrochemical Properties of (MgCoNiZnLi)O Based High Entropy Oxides for Li-Ion Batteries

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Abstract: High entropy oxides (HEOs) are attractive as a negative electrode material for lithium-ion batteries (LIBs), because of the high specific capacities and cycling stabilities. Moreover, they offer a wide range of compositional variation to reach the desired electrochemical performances. In this study, we synthesized the $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ high entropy oxides using conventional solid state reaction technique and examined their electrochemical properties in lithium-ion cells as anode material. The structural properties of as-synthesized high entropy oxides were investigated using X-ray diffraction (XRD) technique, which showed that all the oxides have single-phase rock-salt structure. The increase in the Co content from 5% to 35%, the high entropy oxide based anodes resulted in improved discharge capacity due to the different oxidation states in Co ions. This work indicates that the compositional and elemental valences are very crucial to design and achieve novel high performance high entropy oxide based anode materials for lithium-ion batteries.

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

Introduction

As promising energy storage devices, lithium-ion batteries (LIBs) have attracted much attention due to their high energy density and long cycle life properties. However, to meet the increasing energy and performance expectations in applications such as electric vehicles, energy densities of LIBs should be increased (Puthusseri et al., 2018; Yuan et al., 2014). Thus, the developing high-voltage cathodes and high-capacity anodes is the easiest way to achieve these expectations. Conversion-reaction-based anode materials, especially transition metal oxides are very promising because of their high theoretical capacity and low cost (Yu et al., 2018; Lu et al., 2018).

Since the day it was discovered, the concept of high entropy materials (HEMs) has led to the designing of many new compounds such as high entropy carbides, nitrides, borides, sulfides and oxides. The key concept of HEMs is to use multiple constituents (usually five or more with the concentration of each constituent being between 5 and 35 at. %), in order to maximize the configurational entropy ($S_{config} \geq 1.5R$) to achieve a single phase solid solution structure (Rost et al., 2015). The configurational entropy can be calculated using the following equation:

$$S_{config} = -R\left[\left(\sum_{i=1}^{N} x_i \ln x_i\right)_{cation\ site} + \left(\sum_{j=1}^{N} x_j \ln x_j\right)_{anion\ site}\right]$$

where, x_i and x_j represent the mole fractions of ions present in the cation and anion sites, respectively, and R is the gas constant (Sarkar et al., 2018).

It is reported that the entropy stabilization results in improved cycling capability in (MgCoNiCuZn)O anode (Sarkar et al., 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). 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. Herein, we synthesized the $Co_x(MgNiZnLi)_{100-x}O$ high entropy oxides to further investigation of their electrochemical properties related to the different presence of Co in the structure.

Materials & Methods

MgO, CoO, NiO, ZnO and Li_2O were mixed homogeneously in the determined molar ratios to get $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ stoichiometry and they milled at 300 rpm for 2 h by using the planetary ball mill (Fritsch Pulverisette 7 Premium Line). The obtained oxide mixtures were then unaxially pressed at 300 MPa. Finally, the oxide pellets were sintered at 1000ºC for 12 h prior to the air quenching. The sintered pellets were re-milled at 200 rpm for 1 h to prepare electrodes.

The phase structures of the as-synthesized $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ HEOs were examined by XRD (PANalytical Empyrean) technique using Cu Kα radiation (λ = 0.154 nm). The HEO based anodes were 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 cells were 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 100 mA g^{-1} current density.

Results and Discussion

The XRD patterns of $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ samples, which are prepared by the conventional solid state method, reveal that all the samples have a single phase rock-salt crystal structure. As shown in Figure 1, The diffraction peaks at 2θ values ~36. 92˚, 42. 89˚, 62. 29˚, 74. 63˚ and 78. 56˚, are corresponding to the (111), (200), (220), (311) and (222), planes of the rock-salt crystal structure, respectively.

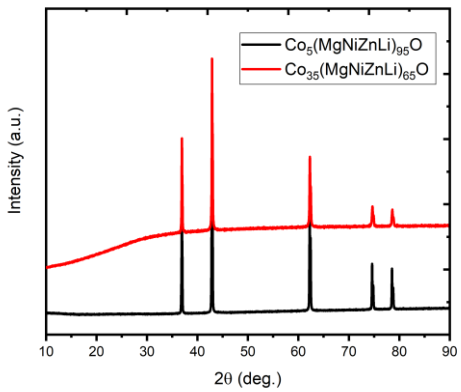

Figure 1. XRD patterns of the as-synthesized $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ HEOs.

Figure 2 shows the galvanostatic initial discharge (Li insertion) voltage profiles of the HEO based anodes at a current density of 100 mA g^{-1} in the voltage window of open circuit voltage (OCV)- 0.01 V. The initial discharge capacities of $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ are 1725 mA h g^{-1} and 1587 mA h g^{-1}, respectively. The discharge plateaus of anodes located around 0.45 V.

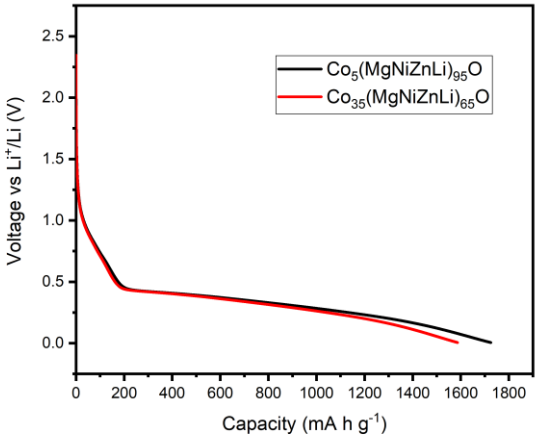

Figure 2. Initial discharge curves of $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ anodes at a current density of 100 mA g^{-1}

The charge-discharge cycles from the 2nd to 5th are given in Figure 3. The discharge voltages of the anodes look slightly increased and the discharge reaction occurs over a potential range of ~1.50-0.01 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.

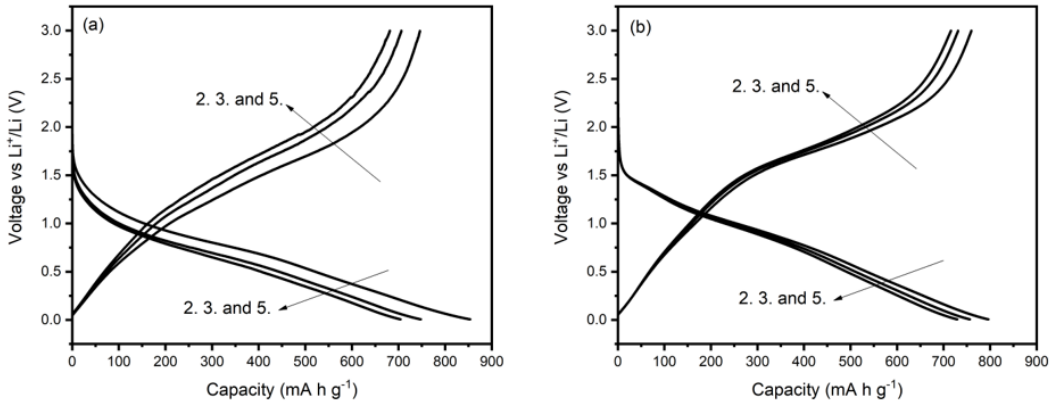

Figure 3. Discharge-charge curves of (a) $Co_5(MgNiZnLi)_{95}O$ and (b) $Co_{35}(MgNiZnLi)_{65}O$ anodes for the 2nd, 3rd and 5th cycles in the voltage range of 0.01-3.00 V at a current density of 100 mA g^{-1}.

The discharge capacities of the $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ anodes are 704 mA h g^{-1} and 729 mA h g^{-1}, respectively at the end of 5th cycle. The cycling stability of $Co_{35}(MgNiZnLi)_{65}O$ anode is relatively better than $Co_5(MgNiZnLi)_{95}O$ anode. Between the 2nd and 5th cycles, the capacity retention of $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ anodes are 82% and 91%, respectively. Therefore, these results evidence that the electrochemical performances of HEO based anodes can be improved by simply changing the cation contents in the structure.

Conclusion

In this work, $Co_5(MgNiZnLi)_{95}O$ and $Co_{35}(MgNiZnLi)_{65}O$ anodes were synthesized with a single-phase rocksalt crystal structure by the conventional solid-state method and their electrochemical performances were observed in the LIB. The results prove that Co content plays an important role in the HEO structure, which affects the

electrochemical performances of anodes. The electrochemical performance of high Co content anode is very satisfactory and promising for the future LIB applications.

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