

## Effect of Mg 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 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  $Mg_x(CoNiZnLi)_{100-x}O$  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  $Mg_5(CoNiZnLi)_{95}O$  and  $Mg_{35}(CoNiZnLi)_{65}O$  HEOs were investigated using X-ray diffraction (XRD) technique, which showed that all the oxides have single-phase rock-salt structure. When tested as anode material in lithium-ion cell,  $Mg_5(CoNiZnLi)_{95}O$  anode exhibits higher initial discharge capacity than  $Mg_{35}(CoNiZnLi)_{65}O$  electrode. However, the  $Mg_{35}(CoNiZnLi)_{65}O$  electrode shows the higher cycling stability than  $Mg_5(CoNiZnLi)_{95}O$  electrode at the further cycle period. This work offers an approach to control the electrochemical properties of HEO based anodes by tuning active and inactive cation contents in the structure.

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

### Introduction

Recently, lithium-ion batteries (LIBs) have been regarded as the main technology for powering portable devices and consumer electronics. Commercial LIBs, based on intercalation type electrodes, such as graphite and  $Li_4Ti_5O_{12}$ , are generally stable, but they have low specific energy (Lu et al., 2018). Therefore, the development of new type electrode materials with high specific energy is very important and necessary. Metal oxides, such as  $MoO_2$ ,  $Co_3O_4$ ,  $MnO$  and  $NiFe_2O_4$  etc. are alternative electrodes for LIBs that working through conversion reactions (Puthusseri et al., 2018; Fang et al., 2019). These reactions are associated with much higher energy densities than intercalation reactions. However, they often suffer from huge volume changes during charge/discharge and have poor cycling stability (Yuan et al., 2014).

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 ( $S_{conf} \geq 1.5R$ ) to achieve a single phase solid solution structure (Rost et al., 2015).

Recently, designing of a high entropy oxide (HEO) to be used as an anode material is considered as one of the important developments in the LIBs. It is reported that the entropy stabilization results in improved cycling capability in (MgCoNiCuZn)O anode (Sarkar et al., 2018). The stable capacity value of  $920 \text{ mA h g}^{-1}$  was reached after 300 cycles upon synthesis of (MgCoNiCuZn)O HEO anode in the form of nanoparticles (Qiu et al., 2019). In another study,  $(MgCoNiZn)_{1-x}Li_xO$  HEOs were synthesized and their electrochemical

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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  $(\text{MgCoNiZn})_{1-x}\text{Li}_x\text{O}$  HEO based anodes, on the structure (Lökçü et al., 2020). They reported the  $(\text{MgCoNiZn})_{0.65}\text{Li}_{0.35}\text{O}$  anode had  $1930 \text{ mA h g}^{-1}$  initial and  $610 \text{ mA h g}^{-1}$  stable discharge capacities. These results were very promising for the use of HEOs as anode material in LIBs. Herein, we synthesized the  $\text{Mg}_x(\text{CoNiZnLi})_{100-x}\text{O}$  high entropy oxides to further investigation of their electrochemical properties related to the different presence of Mg in the structure.

## Materials & Methods

$\text{MgO}$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{ZnO}$  and  $\text{Li}_2\text{O}$  were mixed homogeneously in the determined molar ratios to get  $\text{Mg}_5(\text{CoNiZnLi})_{95}\text{O}$  and  $\text{Mg}_{35}(\text{CoNiZnLi})_{65}\text{O}$  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 uniaxially pressed at 300 MPa. Finally, the oxide pellets were sintered at  $1000^\circ\text{C}$  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  $\text{Mg}_5(\text{CoNiZnLi})_{95}\text{O}$  and  $\text{Mg}_{35}(\text{CoNiZnLi})_{65}\text{O}$  HEOs were examined by XRD (PANalytical Empyrean) technique using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ). 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  $80^\circ\text{C}$  for 12 h. The coin cells were assembled in an argon-filled glove box with  $\text{H}_2\text{O}$  and  $\text{O}_2$  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 ( $\text{LiPF}_6$ ) 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.  $\text{Li}^+/\text{Li}$ ) at  $100 \text{ mA g}^{-1}$  current density.

## Results and Discussion

The XRD patterns of  $\text{Mg}_5(\text{CoNiZnLi})_{95}\text{O}$  and  $\text{Mg}_{35}(\text{CoNiZnLi})_{65}\text{O}$  samples, which are prepared by the conventional solid state method, reveal that all the samples have a single phase rock-salt crystal structure and no impurity peaks are detected in Figure 1.

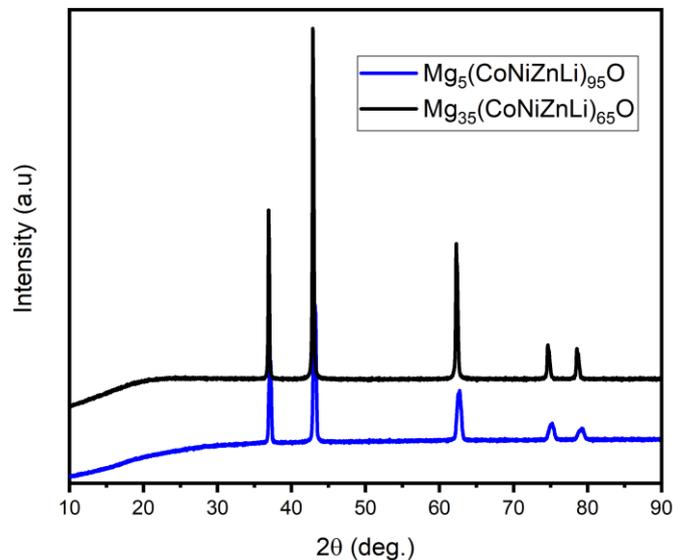


Figure 1. XRD patterns of the as-synthesized  $\text{Mg}_5(\text{CoNiZnLi})_{95}\text{O}$  and  $\text{Mg}_{35}(\text{CoNiZnLi})_{65}\text{O}$  HEOs.

As the amount of Mg increases in the HEO structure, the X-ray diffraction peaks shifts towards lower angle. The shift in XRD peaks is a result of a change in the lattice parameters due to the presence of different amount cations in the HEO structure. Ionic radii of the cations in the rock-salt crystal structure are given in Table 1.

Table 1. Ionic crystal radii of the elements in the rock-salt crystal structure.

Cations	Radius (nm)
Mg <sup>2+</sup>	0.072
Ni <sup>2+</sup>	0.069
Co <sup>2+</sup>	0.075
Co <sup>3+</sup>	0.055
Zn <sup>2+</sup>	0.074
Li <sup>1+</sup>	0.076

The initial discharge capacities of Mg<sub>5</sub>(CoNiZnLi)<sub>95</sub>O and Mg<sub>35</sub>(CoNiZnLi)<sub>65</sub>O are 1459 mA h g<sup>-1</sup> and 1222 mA h g<sup>-1</sup>, respectively. For the initial discharge process, the voltages dropped to a plateau of 0.75 V and 0.32 from the open circuit potential and then decreased to 0.01 V for the Mg<sub>5</sub>(CoNiZnLi)<sub>95</sub>O and Mg<sub>35</sub>(CoNiZnLi)<sub>65</sub>O anodes, respectively. Following the initial discharge curves in Figure 2, the charge-discharge cycles from the 2<sup>nd</sup> to 5<sup>th</sup> are given in Figure 3. The discharge voltages of the anodes look slightly increased and the discharge reaction occurs over a potential range of ~1.38-0.01 V with an inclined single slope. After the first cycle, the significant capacity loss is observed because of the formation of SEI layer at the interface of the electrode surface and the electrolyte and initial lithium loss, mainly due to anode conversion.

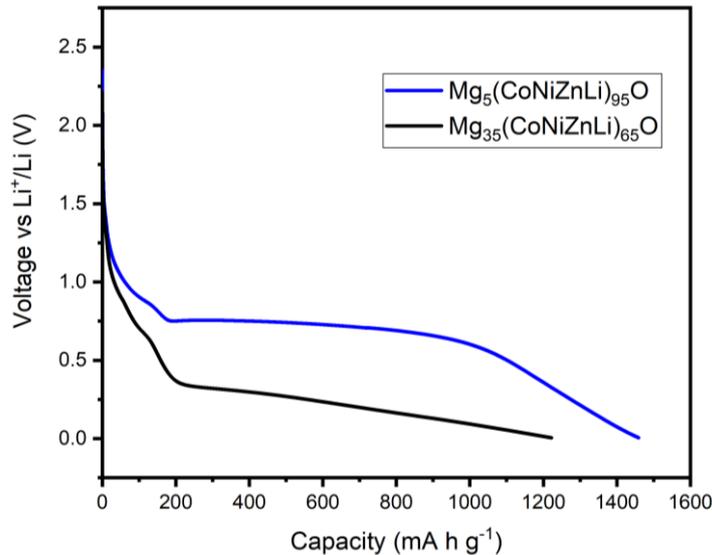


Figure 2. Initial discharge curves of Mg<sub>5</sub>(CoNiZnLi)<sub>95</sub>O and Mg<sub>35</sub>(CoNiZnLi)<sub>65</sub>O anodes at a current density of 100 mA g<sup>-1</sup>.

The discharge capacities of the Mg<sub>5</sub>(CoNiZnLi)<sub>95</sub>O and Mg<sub>35</sub>(CoNiZnLi)<sub>65</sub>O anodes are 168 mA h g<sup>-1</sup> and 576 mA h g<sup>-1</sup>, respectively at the end of 5<sup>th</sup> cycle. The results clearly indicated that increasing content of inactive MgO in the HEO structure promoted the cycling stability of electrode. However, the point to be considered here is that the homogeneous distribution of Mg cation in HEO structure and preserves the rock-salt phase during the charge-discharge process. Otherwise, the mechanical mixture of metal oxides, especially MgO, will not positively contribute to cycling stability of the electrodes.

## Conclusion

Mg<sub>5</sub>(CoNiZnLi)<sub>95</sub>O and Mg<sub>35</sub>(CoNiZnLi)<sub>65</sub>O HEO 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 HEO based Mg<sub>35</sub>(CoNiZnLi)<sub>65</sub>O anode showed excellent cycling stability compared to the Mg<sub>5</sub>(CoNiZnLi)<sub>95</sub>O anode. Therefore, these results evidence that the electrochemical performances of HEO based anodes can be improved by simply changing the active/inactive cation contents in the structure.

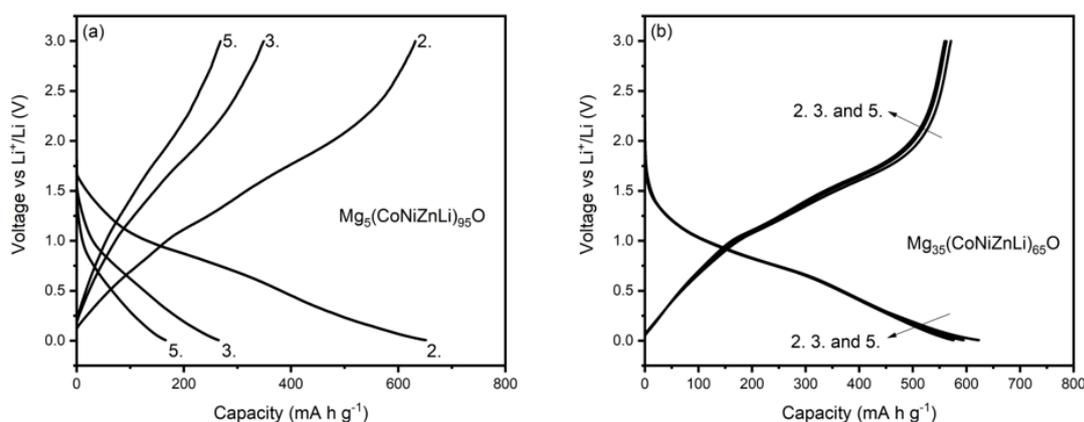


Figure 3. Discharge-charge curves of (a)  $\text{Mg}_5(\text{CoNiZnLi})_{95}\text{O}$  and (b)  $\text{Mg}_{35}(\text{CoNiZnLi})_{65}\text{O}$  anodes for the 2<sup>nd</sup>, 3<sup>rd</sup> and 5<sup>th</sup> cycles in the voltage range of 0.01-3.00 V at a current density of  $100 \text{ mA g}^{-1}$ .

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