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Synthesis and Electrochemical Performance of the $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})$ O High Entropy Oxide as Anode Material for Li-ion Batteries

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Abstract: Presently intercalation type graphite anode electrodes were being used mainly in the commercial Li-ion batteries. Graphite electrodes, however, have reached their theoretical capacity values (≈ 372 $mAhg^{-1}$). Therefore large amount of studies on the synthesis of the novel electrode types were conducted all over the world. One of the novel electrode groups is conversion type electrode. The high entropy design approach is especially utilized in this multi-component oxide electrode synthesis. In this study a new high entropy oxide $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$ was synthesized for the first time in the literature by mixing and grinding of the oxide powders, followed by solid-state reaction at 1000 ºC. The microstructure of the material was characterized using XRD and FESEM-EDX methods, showing single-phase rocksalt structure. The electrochemical performances of the synthesized $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$ as anode material for Li-ion batteries was determined using LIR2016 coin cell. The results showed that $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$, which has good potential to be used as anode in lithium-ion batteries, had the highest capacity value in 1.0 M LiTFSI-DME electrolyte (1725 $mAhg^{-1}$).

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

Introduction

Recently, lithium-ion batteries have been regarded as the main technology for powering portable devices and consumer electronics. Commercial lithium-ion batteries, based on intercalation type electrodes, are generally stable, but they have low specific energy (Puthusseri et al., 2018). Therefore, is very important and necessary to develop new type anode materials with high specific energy. Metal oxides are alternative electrodes for lithium-ion batteries that working through conversion reactions. These reactions are associated with much higher energy densities than intercalation reactions. Simply, the concept of a conversion reaction can be expressed as:

$$M_xO_y + 2yLi^+ + 2ye^- = xM + yLi_2O$$

where, M generally denotes a transition metal. Transition metal oxides can undergo this reaction, yielding high theoretical capacity from 500 to 2000 $mAhg^{-1}$ (Puthusseri et al., 2018; Meister et al., 2016).

Since the day it was discovered, the concept of high entropy alloy (HEA) has led to the emergence of many new materials under the name of high entropy materials (HEMs) such as high entropy carbides, nitrides, borides, sulfides, oxides etc. The key concept of HEMs is to use multiple components (usually five or more in equiatomic amount), in order to maximize the configurational entropy to achieve a single phase, simple solid solution structures. Inspired by this phenomenon, Rost et al. reported the first high entropy oxide (HEO) or entropy stabilized oxide (ESO), which has rocksalt type crystal structure, single-phase solid solution (Mg,Co,Ni,Cu,Zn)O system. Further, many functional and structural properties have been reported for (Mg,Co,Ni,Cu,Zn)O. Berardan et al. reported that (Mg,Co,Ni,Cu,Zn)O possesses promising electrical

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properties. Li-substituted (Mg,Co,Ni,Cu,Zn)O showing larger ionic conductivity because of oxygen vacancies formed due to substitution of a nonisovalent element into the structure. The reaction sequence and mechanical properties of (Mg,Co,Ni,Cu,Zn)O were studied by Hong et al.

Very recently, Sarkar et al. was explored the lithium storage properties of (Mg,Co,Ni,Cu,Zn)O as conversion type anode material for lithium-ion batteries. (Mg,Co,Ni,Cu,Zn)O exhibit reversible lithium storage properties, and it was demonstrated that the improvements in cycling stability are related with entropy stabilization. In another study in which the performance of (Mg,Co,Ni,Cu,Zn)O nanoparticles as an anode material for lithium-ion batteries, which was examined, the electrode with a first discharge capacity of 1585 $mAhg^{-1}$ reached a reversible capacity of 920 $mAhg^{-1}$ after 200 cycles (Chen et al.,2018).

In this work, synthesis and characterization of a new high entropy oxide $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$ was carried out. Furthermore, we studied the anode performance and cycling behavior of synthesized $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$ for lithium-ion batteries in LIR2016 coin cell.

Method

MgO, CoO, NiO, ZnO and Li_2O oxides were mixed with a ball milling (Fritsch Pulverisette 7 Premium Line) for 2 hours at 300 rpm and then uniaxially pressed into pellet under a pressure of 300 MPa. Subsequently, the samples which were heat treated at 1000 °C for 12 hours before air quenching. X-ray Diffraction (XRD) and scanning electron microscopy (SEM) techniques were performed to characterize the synthesized $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$.

For the preparation of electrode, electrode slurry were made by mixing with a ball milling of $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$ powders (70 wt%), Super P acetylene black (20 wt%) and PVDF (10 wt%) in NMP for 3 h at a speed of 300 rpm. The resulting slurries were coated on a Cu foil by brushing and then dried in a vacuum atmosphere at 80 °C for 12 h. LIR2016 coin type cells with a Li metal foil as counter electrode and glass microfiber soaked in 1M LiTFSI:DME as a electrolyte were assembled inside an argon filled glovebox. Discharge/charge tests were performed galvanostatically at 100 mAg^{-1} between the potential range of 0.05-3.00 V (vs. Li^+/Li) by using Gamry Reference 3000 Potentiostat/Galvanostat/ZRA.

Results and Discussion

Fig. 1 shows the (XRD) pattern of a synthesized $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$. The pattern shows that the sample is crystalline and in a form of single phase rocksalt crystal structure. The diffraction peaks at 2θ values 36.8˚, 42.8˚, 62.0˚, 74.5˚ and 78.4˚, are corresponded to the (111), (200), (220), (311) and (222), planes of the rocksalt crystal structure, respectively. A heat treatment temperature of 1000 °C seems to be sufficient for the synthesis of $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$ and additional peaks corresponding to secondary phases is not observed.

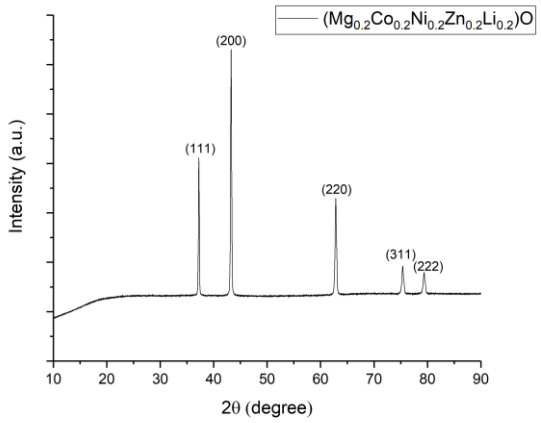

Figure 1. XRD patterns of the $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})$ O sample

The SEM image in Fig. 2 reveals a very dense microstructure for ($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$) O. The sample was successfully sintered at 1000 °C and any pore and secondary phases were not observed in the microstructure. The average grain size of the sample was determined about 1 μm from the SEM observation.

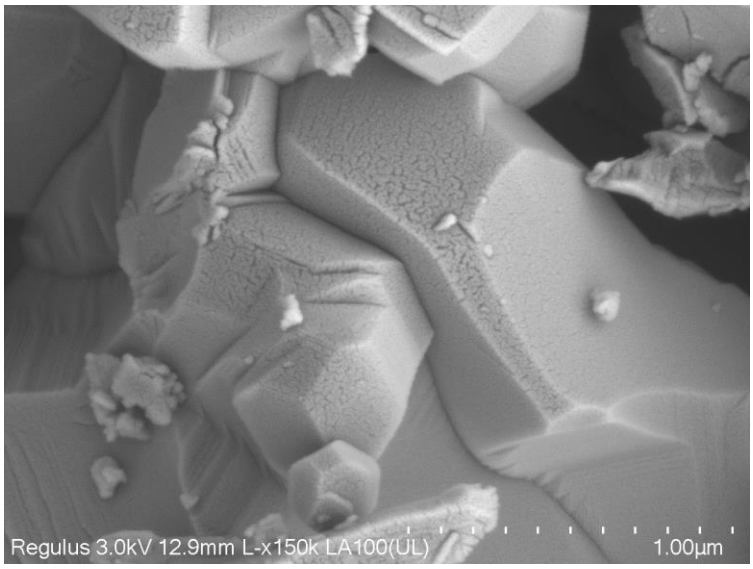

Figure 2. SEM image of the ($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$) O sample

Fig. 3 shows the discharge/charge curves of the ($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$)O anode at a current density of 100 mAg^{-1}. Charging and discharging corresponds to lithiation and delithiation of the ($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$)O anode, respectively. As can be seen from Fig. 3, a specific capacity of about 1725 $mAhg^{-1}$ was achieved in the first discharge with a discharge voltage of ~0.65 V. According to the literature, the ($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$)O anode show a typical voltage profile of metal oxide (Co_3O_4, ZnO, NiO etc.) anode in lithium ion battery for the first discharge process (Lu et al., 2018). It is attributed to the reduction of HEO to Co, Ni, and Zn. After the first cycle, the irreversible capacity loss is observed due to formation of solid electrolyte interphase at the interface of the electrode surface and the electrolyte and initial lithium loss, mainly due to anode conversion (Lu et al., 2018; Chen et al.,2018). On the other hand, after the first cycle, the discharge plateau of the ($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$)O anode were changed at higher potentials and into one slope during the reduction process. A reversible capacity of($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$)O anode is 720 $mAhg^{-1}$ after 10 cycles.

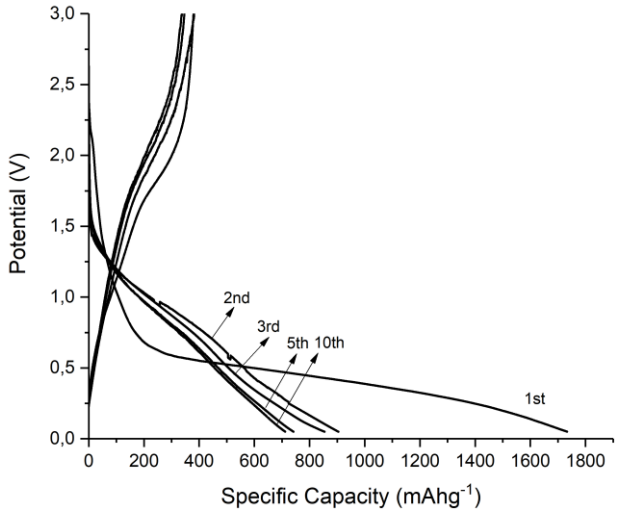

Figure 3. Discharge-charge voltage profiles of ($Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2}$) O for the 1st, 2nd, 3rd, 5th, and 10th cycles in the voltage range of 0.05-3.00 V

Conclusion

In summary, $(Mg_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2}Li_{0.2})O$ high entropy oxide was synthesized and characterized successfully and was applied as a negative electrode material for lithium-ion batteries. A specific discharge capacity of 1725 $mAhg^{-1}$ was observed in the first cycle and maintained at 720 $mAhg^{-1}$ after 10 cycles in LIR2016 coin cell. To determine possible combinations of new HEO based anode materials by revealing the effects of different oxides (cations) on battery performance is highly promising for the future studies.

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