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Study of the Lithium Diffusion Properties of (Mgconilizn)O High Entropy Oxide as an Anode in Lithium-Ion Battery

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Abstract: High-entropy oxide (HEO) based materials have recently significant attention as a conversion type anode material for lithium-ion batteries (LIBs) due to the high specific capacity, cycling stability and rate capability. However, the diffusion kinetics of HEO based anodes for conversion reactions, which occur during the charge and discharge processes have been not studied deeply in the literature. Therefore, the diffusion properties of lithium in the HEO electrodes need to be studied in detail. In this work, the (MgCoNiLiZn)O HEO anode was synthesized by conventional solid-state method. The obtained HEO sample was characterized structurally by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The XRD analysis show that the HEO sample has been successfully synthesized with a single-phase rock-salt structure. The lithium diffusion properties of HEO sample were investigated by various electrochemical techniques including electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

Keywords: High entropy oxide, Lithium diffusion coefficient

Introduction

Rechargeable Li-ion batteries, which have become the main power source for portable electronic devices since the day they were discovered. They are also the most promising systems in the short and medium term for applications where high capacities are required such as electric vehicles. Li-ion battery energy densities have reached around the 300 Wh/kg (18650 type battery configuration); however, studies are continuing rapidly and intensive efforts are being made to increase this value even more (Puthusseri et. al., 2018). In this context, most of the studies have focused on the synthesis of high-performance anode and cathode materials with a high energy density (Etacheri et. al., 2011; Lu et. al., 2018).

One of the main driving forces in materials science is the discovery of new materials with functional properties. The discovery of high entropy alloys in recent years is one of the best examples of this. The discovery of high-entropy alloys has also led to the emergence of many new high-entropy materials such as high-entropy carbide, nitride, boride, sulfur, and oxide (Rost et. al., 2015; Oses et. al., 2020)

Among these high entropy materials, it has been shown that the MgCoNiCuZnO material, which is included in the high entropy oxide class, has high-capacity cycling capability for Li-ion batteries and exhibits a behavior that is significantly different from the classical anode materials. It has been proven that this improvement in cycling ability is due to entropy stabilization (Sarkar et. al., 2018). Following this study, many high entropy

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oxides were synthesized and investigated as anodes for Li-ion batteries. However, the diffusion kinetics of HEO based anodes for conversion reactions, which occur during the charge and discharge processes have been not studied deeply in the literature. In this work, we evaluated the lithium diffusion coefficients of rock-salt type (MgCoNiLiZn)O by using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) techniques.

Materials and Methods

MgO, CoO, NiO, ZnO and Li_2O were mixed homogeneously in the equimolar ratios to get (MgCoNiLiZn)O high entropy oxide and they ball-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 into the pellet of 10 mm diameter at 300 MPa. Finally, the oxide pellet was sintered at 1000ºC for 12 h, and then it was air-quenched. The phase structures and morphologies of the as-synthesized (MgCoNiLiZn)O HEO were examined by XRD and SEM techniques, respectively.

The electrochemical tests of (MgCoNiLiZn)O electrode was performed in lithium half-cell configuration. The electrode was prepared by mixing 75 wt% ball-milled (MgCoNiLiZn)O, 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 by brushing. CV tests were conducted in the voltage range of 0.01-3.0 V vs. Li/Li^+ under different scan rates. EIS measurements were performed with an amplitude of 5.0 mV in the frequency range from 100 kHz to 0.01 Hz.

Results and Discussion

Figure 1 shows the XRD pattern of as-synthesized (MgCoNiLiZn)O sample. The result shows that the sample has a single-phase rock-salt crystal structure. The XRD peaks are given with the MgO reference, which shift due to the presence of five different cations in the structure.

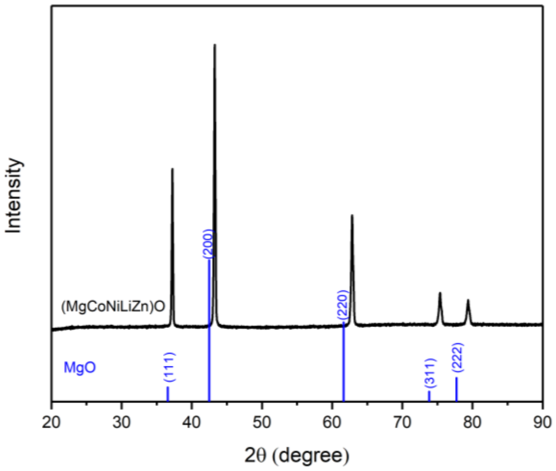

Figure 1. XRD pattern of the (MgCoNiLiZn)O sample

Figure 2 shows typical SEM micrographs of the as-synthesized (MgCoNiLiZn)O sample. The size of the particles ranges from about 0.5 µm to 40 µm. The variable morphological structure of the sample was attributed to the use of the conventional solid-state method in the synthesis process.

CV tests were performed under the different scan rates to investigate the lithium diffusion kinetics in the (MgCoNiLiZn)O electrode. As it is known, the peak current values in the CV curves for cathodic and anodic reactions changes according to the scan rate. This provides a way to understand the diffusion kinetics of lithium at the electrode/electrolyte interface. Figure 3 shows the CV curves with a different scan rate. The relationship and chemical lithium diffusion coefficient can be determined from the Randles-Sevcik equation: (Ding et. al., 2009)

$$i_p = (2{,}69 \times 10^5)\, n^{\frac{3}{2}} A D_{Li^+}^{\frac{1}{2}} C_{Li^+}^{*} v^{1/2}$$

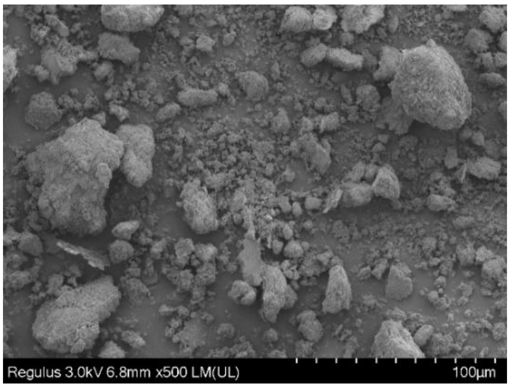

Figure 2. SEM image of the (MgCoNiLiZn)O sample

Where, i_p is the peak current, n is the charge transfer number in (MgCoNiLiZn)O, A is the contact area between electrode and electrolyte, C_{Li}^* is the bulk concentration of lithium in electrode, and ν is the scan rate. The peak current has a linear relationship with the square root of scan rate according to equation.

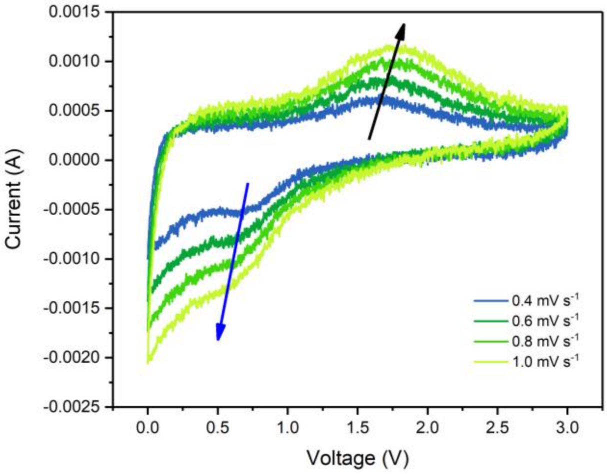

Figure 3. CV curves with a various scan rate of (MgCoNiLiZn)O electrode.

The D_{Li}^+ values calculated at different scan rates of the (MgCoNiLiZn)O electrode is given in Table 1. As seen from the table, The D_{Li}^+ values at different scan rates are in the range of 10^{-13} cm^2 s^{-1}. It has been observed that the diffusion coefficients of similar high entropy oxide-based electrodes changes in the order of 10^{-12} cm^2 s^{-1} -10^{-15} cm^2 s^{-1} in the literature. The high lithium diffusion coefficient in the electrode material indicates that the reaction requirement can be met and better rate performance can be achieved at high current densities.

Table 1. Calculated D_{Li}^+ values of (MgCoNiLiZn)O electrode.

(MgCoNiLiZn)O		Scan rate (mV s^{-1})			
		0.4	0.6	0.8	1.0
D_{Li}^+ (cm^2 s^{-1})	Anodic peak	4.45x10^{-13}	5.11x10^{-13}	5.53x10^{-13}	5.69x10^{-13}
	Cathodic peak	3.52x10^{-13}	4.86x10^{-13}	6.35x10^{-13}	7.58x10^{-13}

Figure 4 presents the Nyquist plot of (MgCoNiLiZn)O electrode. Based on the Warburg impedance, the diffusion coefficient of the lithium ion is calculated through the following equation (Qiu et. al., 2019)

$$D_{Li} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$

Where, R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the charge transfer number in (MgCoNiLiZn)O, F is the Faraday constant, C is the molar concentration of Li^+ in the (MgCoNiLiZn)O and σ is the Warburg coefficient. The σ_w is calculated from the slope of Z' vs. $\omega^{-0.5}$ (ω is the angular frequency) in the Warburg region according to the following equation. The R_s and R_{ct} are solution and charge transfer resistance, respectively.

$$Z' = R_s + R_{ct} + \sigma\omega^{-1/2}$$

The D_{Li}^{+} value of (MgCoNiLiZn)O electrode at the charged state 3.0 V is calculated as 1.88 x10^{-13} cm^2 s^{-1} from EIS datas.

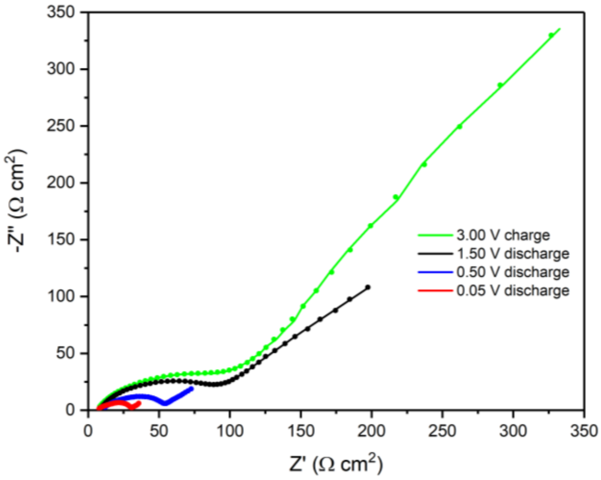

Figure 4. The Nyquist plots of (MgCoNiLiZn)O under different states.

Conclusion

As a conclusion, equimolar (MgCoNiLiZn)O HEO were synthesized with a single-phase rocksalt crystal structure by the conventional solid-state method. In addition, cyclic voltammetry and electrochemical impedance spectroscopy techniques were conducted to evaluate the lithium diffusion coefficient of (MgCoNiLiZn)O electrode. Lithium diffusion coefficients from CV and EIS were in the range of 10^{-13} cm^2 s^{-1}. These values are better than Lithium diffusion coefficients values of many conversions type single transition metal oxides.

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Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

References

Ding, N., Xu, J., Yao, Y.X, Wegner, G., Fang, X., Chen, C.H. & Lieberwirth, I. (2009). Determination of the diffusion coefficient of lithium ions in nano-Si. *Solid State Ionics*. *180*, 222–225.

Etacheri, V., Marom, R., Elazari, R., Salitra, G., & Aurbach, D. (2011). Challenges in the development of advanced Li-ion batteries: a review. *Energy & Environmental Science, 4*(9), 3243.

Lu, J., Chen, Z., Pan, F., Cui, Y., & Amine, K. (2018). High-performance anode materials for rechargeable lithium-ion batteries. *Electrochemical Energy Reviews, 1*, 35−53.

Oses, C., Toher, C., & Curtarolo, S. (2020). High-entropy ceramics. *Nature Reviews Materials, 5*(4), 295-309. https://doi.org/10.1038/s41578-019-0170-8.

Puthusseri, D., Wahid, M., & Ogale, S. (2018). Conversion-type anode materials for alkali-ion batteries: State of the art and possible research directions. *ACS omega*, *3*(4), 4591-4601.

Qiu, N., Chen, H., Yang, Z., Sun, S., Wang, Y., & Cui, Y. (2019). A high entropy oxide (Mg0. 2Co0. 2Ni0. 2Cu0. 2Zn0. 2O) with superior lithium storage performance. *Journal of Alloys and Compounds*, *777*, 767-774.

Rost, C. M., Sachet, E., Borman, T., Moballegh, A., Dickey, E. C., Hou, D., ... & Maria, J. P. (2015). Entropy-stabilized oxides. *Nature communications*, *6*(1), 1-8.

Sarkar, A., Velasco, L., Wang, D. I., Wang, Q., Talasila, G., de Biasi, L., ... & Breitung, B. (2018). High entropy oxides for reversible energy storage. *Nature communications*, *9*(1), 1-9.

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