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Synthesis and Electrochemical Performance of Spinel Crystal Structured $((FeNiCrMn)_{1-x}Co_x)_3O_4$ (x=0.1, 0.2, 0.3) High Entropy Oxides

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Abstract: High entropy oxides are a new class of materials with a single-phase structure consisting of five or more components. Due to their high structural stability and electrochemical performance, they have attracted a lot of attention in recent years. In this study, high entropy oxides with the composition $((FeNiCrMn)_{1-x}Co_x)_3O_4$ (x=0.1, 0.2, 0.3) were synthesized using the solid state method and their electrochemical performances as anode material for lithium-ion battery were investigated. Spinel crystal structured of high entropy oxides were characterized by X-ray diffraction (XRD) technique. The electrochemical performance of anodes were evaluated by assembling CR2016 type coin cell. As a result of galvanostatic charge/discharge experiments the initial discharge capacities of $((FeNiCrMn)_{1-x}Co_x)_3O_4$ (x=0.1, 0.2, 0.3) anodes at a current density of 50 mA g^{-1} were calculated as 1993 mA h g^{-1}, 1651 mA h g^{-1} and 1706 mA h g^{-1}, respectively. Among the synthesized high entropy oxide anodes, the $((FeNiCrMn)_{0.9}Co_{0.1})_3O_4$ anode shows high initial discharge capacity, while their capacity retention rates at the end of 10th cycle were calculated as 53.9%, 55.1%, 59.7%. This study clearly indicates that the electrochemical performances of high entropy oxide anodes are affected by the Co content.

Keywords: High entropy oxide, Spinel crystal structure, Li-Ion batteries

Introduction

Due to the increasing energy demand and environmental issues, many studies have been focused on the development of efficient and renewable energy sources (Shen et. al., 2018). Rechargeable batteries are mainly power sources for electric vehicles. On the other hand, they can be used as energy storage devices. Therefore, they are considered as sustainable energy storage systems (Etacheri et. al., 2011; Lu et. al., 2013). Today, Li-ion batteries are the most widely used rechargeable batteries. The most important advantages of these batteries are their high energy storage capacity and long cycle life (Velàzquez-Martinez et. al., 2019; Kim et. al., 2019).

Graphite is the most commonly used anode material in Li-ion batteries. It has high electronic conductivity and low cost. However, its theoretical capacity is low (372 mA h g^{-1}) (Nitta et. al., 2015; Long et. al. 2017). Another group of anode material is conversion type anodes. Conversion type transition metal oxides show high theoretical capacity but generally suffer from significant volume change and poor electrical conductivity (Zou

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et. al., 2011). In recent years, high entropy oxide based anodes have extensively studied as an alternative to transition metal oxide based anodes.

In 2015, the concept of high entropy oxide was used for the first time. High entropy oxides are a single phase structure consisting of five or more major elements (Rost et. al., 2015). In addition, for the first time in 2018, rock-salt crystal structure $(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$ was used as the anode material in Li-ion batteries, and this oxide compound showed excellent electrochemical performance even at 500 cycles (Sarkar et. al., 2018). In other study $(MgCoNiZn)_{1-x}Li_xO$ (x=0.5-0.35) high entropy oxides were synthesized with different Li^+ concentrations. The increase in Li^+ concentration caused an increase in the oxygen vacancy in Li-ion batteries. This has resulted in an increase in the discharge capacity (Lökçü et al., 2020). In another study spinel $(Mg_{0.2}Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})_3O_4$ anode exhibited a reversible capacity of 504 mA h g^{-1} after 300 cycles at a current density of 100 mA g^{-1} (Chen et. al., 2020).

In this study, $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3) high entropy oxide anode materials were synthesized and their electrochemical performances were investigated in Li-ion batteries.

Materials & Methods

Fe_3O_4, NiO, Cr_2O_3, MnO and CoO oxides were mixed in the specified molar ratios with determined stoichiometry and were ground at 300 rpm for 2 hours using a ball mill (Fritsch Pulverisette 7 Premium Line). Then the obtained oxide mixtures were pressed into pellets with a diameter of 10 mm under a pressure of 300 MPa. Finally, the oxide pellets obtained were sintered at 1100 ° C for 12 hours. X-ray Diffraction (XRD) was used to characterize the synthesized $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3).

$((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3) electrodes were prepared by mixing in a ball mill at NMP using Super P carbon black and PVDF (75:15:10 by weight). The prepared mixture was coated on Cu foil and dried in a vacuum atmosphere at 80 °C for 12 h. Anode materials are electrochemically tested in a CR2016 type coin cells. The coin cells were assembled in an argon-filled glove box with H_2O and O_2 levels less than 0.1 ppm. Lithium metal was used as the counter and reference electrode, while the glass microfiber filter was used as a separator. As the electrolyte, 1 M Lithium hexafluorophosphate ($LiPF_6$) was used in EC: DMC in a ratio of 1:1 by volume. Charge-discharge tests were performed galvanostatically in the potential range of 0.01 and 3.00 V (vs. Li^+/Li) at a current density of 50 mA g^{-1} by using Gamry Reference 3000 Potentiostat/Galvanostat/ZRA.

Results and Discussion

Figure 1 shows the XRD pattern of a synthesized $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3). The patterns show that the samples are crystalline and spinel crystal structure. These characteristic peaks of the spinel structure, (111), (220), (311), (222), (400), (422), (511), (440), (531), (620), (533), (622), (444), (711) and (642) planes. A heat treatment temperature of 1100 °C seems sufficient for the synthesis of $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3) samples.

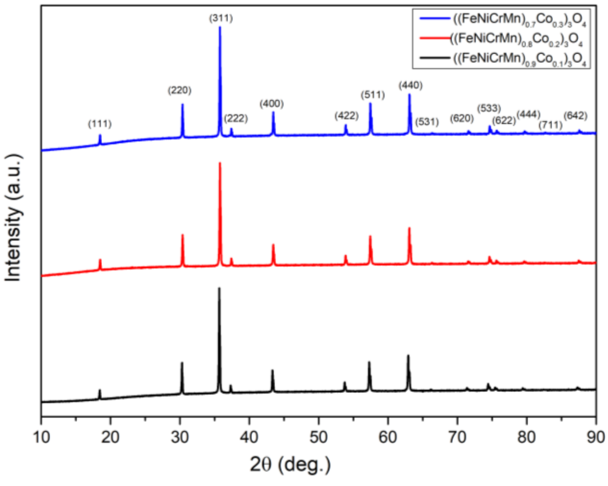

Figure 1. XRD patterns of the as-synthesized $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3) samples.

The first charge-discharge curves of the anodes are given in Figure 2. When the initial discharge curves are examined, a discharge plateau is observed at approximately 0.5 V. This plateau represents the reduction of metal oxides and the formation of the SEI layer. The initial discharge capacities of $((FeNiCrMn)_{0.9}Co_{0.1})_3O_4$, $((FeNiCrMn)_{0.8}Co_{0.2})_3O_4$ and $((FeNiCrMn)_{0.7}Co_{0.3})_3O_4$ anodes are 1993 mA h g^{-1}, 1651 mA h g^{-1} and 1706 mA h g^{-1}, respectively. The initial charge capacities of $((FeNiCrMn)_{0.9}Co_{0.1})_3O_4$, $((FeNiCrMn)_{0.8}Co_{0.2})_3O_4$ and $((FeNiCrMn)_{0.7}Co_{0.3})_3O_4$ anodes are 1381 mA h g^{-1}, 1191 mA h g^{-1} and 1203 mA h g^{-1}, respectively. In addition, the initial coulombic efficiencies are 70.5%, 72.1% and 69.3%, respectively. The low initial coulombic efficiencies are due to the reaction caused by the SEI film.

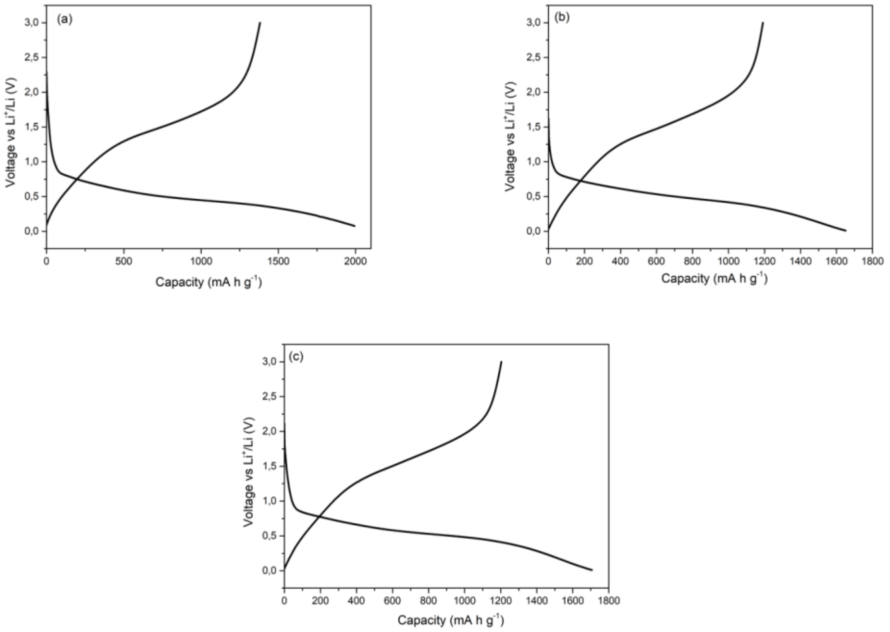

Figure 2. Discharge-charge curves of (a) $((FeNiCrMn)_{0.9}Co_{0.1})_3O_4$, (b) $((FeNiCrMn)_{0.8}Co_{0.2})_3O_4$ and (c) $((FeNiCrMn)_{0.7}Co_{0.3})_3O_4$ anodes for the first cycle in the voltage range of 0.01 - 3.00 V at a current density of 50 mA g^{-1}.

Cycling performance of the $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3) anodes under 50 mA h g^{-1} current density is shown in Figure 3. The $((FeNiCrMn)_{0.9}Co_{0.1})_3O_4$, $((FeNiCrMn)_{0.8}Co_{0.2})_3O_4$ and $((FeNiCrMn)_{0.7}Co_{0.3})_3O_4$ anodes deliver capacities of 1075 mA h g^{-1}, 909 mA h g^{-1} and 1018 mA h g^{-1} at 50 mA g^{-1} current densities and at the end of the 10th cycle, respectively. At the end of the 10th cycle, the coulombic efficiencies of the anodes are 95.7%, 96.5% and 97.2%, respectively. Between the 1st and 10th cycles, the capacity retention of $((FeNiCrMn)_{0.9}Co_{0.1})_3O_4$, $((FeNiCrMn)_{0.8}Co_{0.2})_3O_4$ and $((FeNiCrMn)_{0.7}Co_{0.3})_3O_4$ anodes are 53.9%, 55.1% and 59.7%, respectively. These results show that the electrochemical performances of high entropy oxide anodes are affected by the Co content.

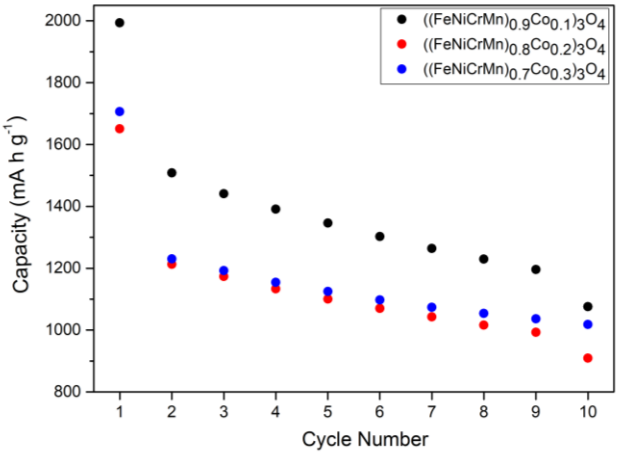

Figure 3. Cycling performance of $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3) anodes under current density at 50 mA g^{-1}.

Conclusion

In this work, $((FeNiCrMn)_xCo_{1-x})_3O_4$ (x=0.1, 0.2, 0.3) anodes were synthesized with a spinel crystal structure by the conventional solid-state method and their electrochemical performances were observed in the Li-ion batteries. Charge-discharge measurements showed that the $((FeNiCrMn)_{0.9}Co_{0.1})_3O_4$ anode delivers a high initial discharge capacity of 1993 mA h g^{-1} and reversible capacity of 1075 mA h g^{-1} at the end of 10th cycle. It was observed that the capacity retention rate of the cell increased depending on the increase in the amount of Co. These capacity values are quite promising as alternative anode material for Li-ion batteries.

Scientific Ethics Declaration

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

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