

High-Entropy Oxides for Energy Storage Systems: Role of Crystalline Structure and Defects in Alkali Metal-Ion Battery Storage Mechanisms.

Claudia Triolo, Saveria Santangelo

Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM), Università degli Studi "Mediterranea" di Reggio Calabria, 89122 Reggio Calabria, Italy

In the latest years, high-entropy materials (HEMs) have attracted growing interest for their great potential in a broad range of applications, spanning from catalysis to energy storage and conversion systems. HEMs are defined as single-phase solid solution in which five or more metals are present in equimolar concentration and they are randomly distributed in the lattice. The HEM family includes alloys (HEAs) and oxides (HEOs) that can give rise to many kinds of crystalline structures, such as rock-salt, spinel, perovskite and fluorite. The interest in the HEM is due to their structural and electrochemical activity that can be easily changed varying the metal composition and the treatment conditions.

This work concerns the preparation of HEO through two synthesis methods and their structural and electrochemical analysis: nanoparticles (NPs) have been produced by the sol-gel method, while nanofibers (NFs) have been obtained by electrospinning technique. Both procedures require a post thermal treatment in air. Comparing the obtained HEO crystallites reveals how their morphology and crystalline quality are influenced by the synthesis process and thermal treatment. Additionally, the specific combination of metals in HEOs plays a key role in determining the crystalline structure of the material. Spinel and rock-salt structures have been widely studied as active anode materials in lithium ion batteries (LIBs). In this context, our studies focused on the investigation of HEOs based on (MgCoNiCuZn), which give rise to rock salt structure, and (Cr,Mn,Fe,Co,Ni) and (MnFeCoNiZn) combinations that create a spinel structure. The (MgCoNiCuZn)-HEO exhibit outstanding electrochemical properties in terms of reversible capacity (480 mAh/g at 20 mA/g), rate capability (206 mAh/g at 2 A/g) and cycling stability (390 mAh/g at 0.5 A/g after 300 cycles), due to the stabilizing action of Mg. The spinel HEO based on (MnFeCoNiZn) exhibit long-term stability (453 mAh/g after 550 cycles at 0.5 A/g) and rate-capability (210 mAh/g at 2 A/g). However, further improvements are possible, as demonstrated for (MnFeCoNiZn)-HEO, where the insertion of Li into the HEO structure and the formation of carbon/HEO composites allowed to improve the stability, ionic transport and mechanical stability of the electrodes for LIBs.

Interestingly, HEO have been also incorporated as filler into a polyethylene oxide (PEO) matrix to obtain HEO@PEO composites, which have been successfully used in solid composite electrolytes for LIBs, improving its ionic conductivity and anodic stability window of the pristine polymer.



Dr. Claudia Triolo received her Master's degree in Condensed Matter Physics in 2012 and her Ph.D. in Physics from the University of Messina in 2016. Since 2019, she has been a Researcher at the University "Mediterranea" of Reggio Calabria. Her research focuses on the design and application of scanning probe microscopy techniques, standard optical characterization methods, Raman spectroscopy, and near-field analysis of the plasmonic behavior of metallic nanostructures. More recently, her work has expanded to include the chemical synthesis of metal oxide nanoparticles—including high entropy oxides—for electrochemical applications.