High-Entropy Sn$_{0.8}$(Co$_{0.2}$Mg$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)$_{2.2}$O$_{4}$ Conversion-Alloying Anode Material for Li-Ion Cells: Altered Lithium Storage Mechanism, Activation of Mg, and Origins of the Improved Cycling Stability

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ABSTRACT: Benefits emerging from applying high-entropy ceramics in Li-ion technology are already well-documented in a growing number of papers. However, an intriguing question may be formulated: how can the multicomponent solid solution-type material ensure stable electrochemical performance? Utilizing an example of nonequimolar Sn-based Sn$_{0.8}$(Co$_{0.2}$Mg$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)$_{2.2}$O$_{4}$ high-entropy spinel oxide, we provide a comprehensive model explaining the observed very good cyclability. The material exhibits a high specific capacity above 600 mAh g$^{-1}$ under a specific current of 50 mA g$^{-1}$ and excellent capacity retention near 100% after 500 cycles under 200 mA g$^{-1}$. The stability originates from the conversion-alloying reversible reactivity of the amorphous matrix, which forms during the first lithiation from the initial high-entropy structure, and preserves the high level of cation disorder at the atomic scale. In the altered Li-storage mechanism in relation to the simple oxides, the unwanted aggregated metallic grains are not exsolved from the anode and therefore do not form highly lithiated phases characterized by large volumetric changes. Also, the electrochemical activity of Mg from the oxide matrix can be clearly observed. Because the studied compound was prepared by a conventional solid-state route, implementation of the presented approach is facile and appears usable for any oxide anode material containing a high-entropy mixture of elements.

KEYWORDS: Li-ion cells, anodes, conversion and alloying reactions, high-entropy oxides, cycling stability, Li-storage mechanisms

1. INTRODUCTION

Nowadays, to construct fast-charging batteries with the desired high capacity and optimal operating voltage, as well as improved safety, the state-of-the-art intercalation-based graphite anode must be replaced by anodes with different chemistries operating based on new principles.1−3 Together with the implementation of new kinds of anodes, undoubtedly leading to substantial progress in the field of Li-ion batteries, many new challenging issues related to the different working mechanisms have emerged, making the actual commercialization of these materials limited almost only to composites with a small addition of Si, reversibly forming lithium intermetallics.3−6 In a search for a further improvement of the anodes' electrochemical performance, it was proposed a few years ago to combine the alloying and conversion Li-storage mechanisms within a single compound (conversion-alloying materials, CAMs), benefiting from their advantages and confining the disadvantages7,8 (details of the idea of the CAM approach and its characteristics can be found in Supplementary Note 1).

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Despite overall improved electrochemical properties of CAMs, their poor cycling stability, mainly due to severe volumetric changes intrinsically related to both constituent types of reaction with Li, appears as the main limitation. As of today, the performance of CAM-based anodes in Li-ion cells is governed by the architecture of the particles and electrode, requiring rather expensive, sophisticated synthesis methods and/or carbonaceous additives. From another perspective, the most recent reports show that a novel group of materials, the so-called high-entropy oxides (HEOs), exhibits very promising electrochemical properties considering their use as cathodes and anodes in Li-ion cells. HEOs are regarded as multiprincipal component solid solutions characterized by high configurational entropy. The materials show significantly enhanced solubility limits and excellent structural stability, with most of the exceptional properties emerging from synergistic effects, beyond a simple rule of mixing. When the HEO-based anodes are compared, all have one thing in common: regardless of the synthesis method and resulting morphology, they always exhibit remarkable cycling stability, which distinguishes them from conventional analogues. The observed excellent cycling performance of HEOs is attributed, at least to some degree, to the influence of the high entropy on the phase stabilization. However, until now, it has not been properly addressed how exactly the entropy can stabilize phases in the ongoing electrochemical process, which leads to a decomposition of the initial structure. The current state of knowledge on the electrochemical working mechanisms of HEOs is summarized in Supplementary Note 2.

In our work, we have developed a novel concept of applying the high-entropy approach to CAMs, aiming for the creation of anode materials for Li-ion batteries characterized by excellent cycling stability, as well as good electrochemical performance, and most importantly, obtained using a simple synthesis method, without expensive additives. Utilizing an easily scalable solid-state route, we synthesized the spinel-structured $\text{Sn}_0.3(\text{Co}_{0.2}\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_2\text{O}_4$ anode material, whose electrochemical properties significantly outperform conventional spinel-type CAMs. This allowed incorporating desired amounts of the respective elements into the anode material, being also homogenously distributed at the atomic level. We also explain the Li-storage mechanisms and origins of the reported very good cyclability, involving reversible lithiation of the amorphous matrix containing all the components well-mixed at the atomic scale, including electrochemically active Mg.

### 2. EXPERIMENTAL SECTION

#### 2.1. Synthesis

The Sn-rich samples, $\text{SnO}_2(\text{Co}_{0.2}\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_2\text{O}_4$ (further denoted as Sn0.8-MES) and $\text{Sn}(\text{Co}_{0.3}\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_2\text{O}_4$ (further denoted as Sn1-MES) HEOs, as well as the SnZn$_{0.12}$O$_{3-x}$ reference material, were synthesized using a typical solid-state method. The following reactants were mixed in the selected stoichiometric proportions: $\text{SnO}_2$ (Alfa Aesar, 99.9%), $\text{CoO}_2$ (Alfa Aesar, 99.995%), $\text{MgO}$ (Alfa Aesar, 99.995%), $\text{MnO}$ (Alfa Aesar, 99.99%), $\text{NiO}$ (Alfa Aesar, 99.998%), and $\text{ZnO}$ (Alfa Aesar, 99.9%). The powders were mixed in isopropyl alcohol for 20 min in a high-energy ball mill Spex SamplePrep 8000 M using zirconia balls and subsequently dried. The ball-to-powder weight ratio was ca. 3:1. The obtained precursors were formed into 10 mm diameter pellets using a uniaxial hydraulic press under a pressure of 250 MPa. The green bodies were then free-sintered at 1200 °C for 20 h followed by cooling down to room temperature with a furnace.

The as-obtained sinters were ground with an agate mortar into powders. In some cases, there was an additional step including another pelleting and sintering under the same conditions.

#### 2.2. Characterization (XRD, SEM, DLS, TEM/HR-TEM/STEM/EDS/SAED, Raman Spectroscopy, Mössbauer Spectroscopy, and XPS)

The as-obtained ground powders were characterized by the X-ray diffraction (XRD) method conducted in 0–θ Bragg–Brentano geometry using a Panalytical Empyrean diffractometer with CuKα radiation equipped with a PIXcel3D detector within the 10–110° range at room temperature. The typical measurement lasted for 51 min with a resolution of 0.013°. Panalytical HighScore software (ICDD PDF4+ 2021 database) was used for qualitative phase analysis. Quantitative analysis of XRD data was performed using Rietveld refinements using GSAS-II. Morphology and chemical composition of the oxides were investigated using scanning electron microscopy (SEM) in secondary electrons (SEs) and/or backscattered electrons (BSEs) combined with energy-dispersive X-ray spectroscopy (EDS) analysis using a ThermoFisher Scientific Phenom XL Desktop SEM equipped with a silicon drift detector. The applied accelerating voltage was 15 kV. Raman spectroscopy studies were performed at room temperature on a Thermo Scientific DXR3 Raman Microscope using a 532 nm green laser, 1800 grooves/mm grating, and a working distance objective (objective curvature: 100 mm, 5.0 cm$^{-1}$ resolution). The current state of knowledge on the electrochemical working mechanisms of HEOs is summarized in Supplementary Note 2. In our work, we have developed a novel concept of applying the high-entropy approach to CAMs, aiming for the creation of anode materials for Li-ion batteries characterized by excellent cycling stability, as well as good electrochemical performance, and most importantly, obtained using a simple synthesis method, without expensive additives. Utilizing an easily scalable solid-state route, we synthesized the spinel-structured $\text{SnO}_2(\text{Co}_{0.2}\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_2\text{O}_4$ anode material, whose electrochemical properties significantly outperform conventional spinel-type CAMs. This allowed incorporating desired amounts of the respective elements into the anode material, being also homogenously distributed at the atomic level. We also explain the Li-storage mechanisms and origins of the reported very good cyclability, involving reversible lithiation of the amorphous matrix containing all the components well-mixed at the atomic scale, including electrochemically active Mg.

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an electrode was prepared by mixing the active material, Timcal Graphite & Carbon Super P (MTI Corporation), and poly(vinylidene fluoride) binder (PVDF, HSV900 Arkema) in 70:20:10 weight ratio in N-methyl pyrrolidone (NMP, Alfa Aesar, 99.5%) using a high-speed homogenizer Polytron PT 2500 E to obtain a slurry. The obtained mixture was coated on a Cu foil (12 μm thick, MTI Corporation) via the doctor blade method and then dried. The mass loading of the active material was in a range of 1.5−2.0 mg cm$^{-2}$.

Subsequently, CR2032 coin half-cells with Li foil (0.75 mm thick, Alfa Aesar, 99.9%) as the counter electrode, glass microfiber (Whatman) and polymer Celgard separators, and commercial electrolyte (1 M LiPF$_6$ in 1:1 (v/v) ethylene carbonate (EC): diethyl carbonate (DEC), Sigma Aldrich) were assembled inside an Ar-filled glovebox (UNILab MBraun, Ar, H$_2$O < 0.1 ppm, O$_2$ < 0.1 ppm). The obtained batteries were analyzed electrochemically through the galvanostatic charge/discharge (GDC), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) techniques on a Biologic VMP3 electrochemical workstation. All the measurements were conducted at 23 °C in a thermostat. The specific capacities and currents were calculated taking into account the mass of the active material.

![Figure 1. Structural studies of Sn0.8-ME5: (a) XRD data with Rietveld refinement assuming partial (0.05) transfer of Sn to tetrahedral positions, $R_{wp} = 2.82\%$, for all Sn in octahedral sites $R_{wp} = 2.96\%$ (not shown); minor amount of the rock salt-structured second phase is marked with black squares; Miller indices correspond to the spinel phase (Fd-3m), $a$ is the lattice parameter, and $R_{wp}$ is the weighted profile R-factor of the refinement. (b) Raman spectrum for Sn0.8-ME5 (mean from 10 measurements at different positions on the sample’s surface) compared with a measured spectrum for conventional SnZn$_2$O$_4$; vibrational modes assigned based on ref 41. (c,d) HR-TEM image measured for manually ground powder (c), and the zoomed region (d) with the inset showing the corresponding FTT pattern with indexed spots assigned to the spinel structure, [110] zone axis. (e) Room-temperature $^{119}$Sn Mössbauer spectrum fitted assuming one quadrupole doublet with the calculated parameters presented in Table S2 and difference spectrum at the top, together with the quadrupole splitting distribution curve. (f) XANES spectra for Mg K-edge and Mn, Co, Ni, Zn L$_\text{3}$-, and L$_\text{2}$-edges measured in PFY mode with reference spectra for simple oxides from the literature.$^{46−50}$ (g) STEM image with the corresponding EDS map showing the uniform distribution of elements, measured for manually ground powder. (h) SEM image with the corresponding EDS map measured on a gently polished pellet’s cross-section.

![XRD data with Rietveld refinement](image1.png)

![Raman spectrum](image2.png)

![HR-TEM image](image3.png)

![Mössbauer spectrum](image4.png)

![XANES spectra](image5.png)

![STEM image](image6.png)

![SEM image](image7.png)
For the preparation of optimized electrodes, the same Sn0.8-ME5 powder (manually ground for 30 min) was mixed with Timcal Graphite & Carbon Super P (MTI Corporation), carboxymethyl cellulose (CMC, MTI Corporation), and styrene-butadiene rubber (SBR, 48 wt % water solution, MTI Corporation) in 70:20:5:5 or 65:25:5:5 ratio in deionized water overnight. The mass loading of the active material was in a range of ca. 7 mg cm$^{-2}$. Subsequently electrodes of 8 mm diameter were punched out. The slurry was spread onto carbon-coated copper TEM grids. In the case of Sn0.8-ME5 oxide was ultrasonicated in isopropyl alcohol and prepared by drop-casting on carbon-coated copper TEM grids. In the case of Mössbauer spectroscopy, samples together with a Pb mask were sealed with Kapton tape and embedded in epoxy resin. All the samples were transferred to the respective apparatus in sealed bags under an Ar atmosphere to prevent oxidation.

2.5. Operando XRD and EIS Measurements. For the operando XRD measurements, the self-supported electrode layers were prepared by mixing Sn0.8-ME5 powder, Timcal Graphite & Carbon Super P, and PVDF (70:10:20 ratio) in acetone as a solvent. The amount of binder within the self-standing electrode layer was increased compared with a typical electrode on a Cu foil to avoid cracking during cell’s assembly and battery work. The slurry was spread onto the glass support via the doctor blade method and dried in air. Subsequently electrodes of 8 mm diameter were punched out. The loading of the active material was in a range of ca. 7 mg cm$^{-2}$. The prepared electrodes were assembled with a Li counter electrode, a glass microfiber separator (Whatman), and a commercial electrolyte (1 M LiPF$_6$ in 1:1 (v/v) EC:DEC). A custom-made electrochemical cell with a beryllium window, compatible with a Planalytical Empyrean diffractometer (the same as described in Section 2.2.). The experiment was conducted during the first charge/discharge cycle using a one-channel Biologic potentiostat/galvanostat with a specific current of 30 mA g$^{-1}$ and a long-term ex situ SEM studies for which the charge/discharge conditions are described in the text), and disassembled in the Ar-filled glovebox. In the case of TEM, SEM, and XAS measurements, to ensure optimal experimental conditions, the electrodes after disassembling were soaked in DEC electrolyte solvent. For TEM studies, ex situ samples were ultrasonicated in isopropyl alcohol and prepared by drop-casting on carbon-coated copper TEM grids. In the case of Mössbauer spectroscopy, samples together with a Pb mask were sealed with Kapton tape and embedded in epoxy resin. All the samples were transferred to the respective apparatus in sealed bags under an Ar atmosphere to prevent oxidation.

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3. RESULTS
3.1. Structure of the New Sn$_{0.8}$(Co$_{0.2}$Mg$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)$_2$O$_{4}$ HE0 Spinel. Numerous inverse 4-2 spinels with a general formula [A]$^+$[tetrahedral][A]$^{2+}$[octahedral]$_2$O$_4$ are known, in which +2 cations from the 3d metals group (as well as Mg$^{2+}$) are present in both the tetrahedral and the octahedral sites. Because the B$^{4+}$ cation can be Sn$^{4+}$, this naturally gives rise to a group of spinel-type CAMs, in which a favorable ratio between tin, working on a basis of the alloying reaction with Li, and selected 3d metal A$^{2+}$ cations showing (typically) the conversion-type reactivity, is present. The B$^{4+}$:A$^{2+}$ ratio, equal to 1:2, seems vital for the reported very good electrochemical performance of such CAMs. Bearing in mind that A$^{2+}$ can be selected among many ions, this allows for an easy implementation of the high-entropy approach. More details about the selection of the discussed system and the reactivity of chosen elements with Li can be found in Supplementary Note 3.

Initially, we attempted to maintain the stoichiometric spinel composition and synthesize Sn(Co$_{0.2}$Mg$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)$_2$O$_4$ HE0 (further denoted as Sn1-MES), using a conventional solid-state route. However, the XRD data showed that while the sample contained the majority of the desired Fd-3m spinel phase, the precipitated SnO$_2$ phase could be clearly observed. To eliminate this unwanted phase, we synthesized a composition with the tin deficiency (in relation to the conventional 4-2 Sn-based spinels), Sn$_{0.8}$(Co$_{0.2}$Mg$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)$_2$O$_4$ (further denoted as Sn0.8-ME5). The XRD pattern with performed Rietveld refinement for the material (Figure 1a) shows that we successfully obtained the spinel-structured HE0, with only a negligible amount of the rock salt-structured secondary phase (3.3 wt %). A more detailed description of the phase composition of Sn0.8-ME5 and Sn1-MES is provided in Supplementary Note 4, Figure S1, and Table S1. Interestingly, a better Rietveld fit could be obtained assuming a small amount of tin present also in tetrahedral positions, indicating an increasing cation disorder and a partial transformation toward random spinel.

Comprehensive TEM, Raman, and $^{119}$Sn Mössbauer spectroscopy studies allowed describing the structural features of the considered Sn0.8-ME5 HE0. The bands visible in the Raman spectrum correspond to the spinel-type structure, with five active modes typical of the Fd-3m space group (Figure 1b). However, large broadening as well as the emergence of additional peaks suggests a high level of cation disorder and structural distortion (Supplementary Note 5). The presence of the spinel-type structure is further proven by the HR-TEM, with all the observed spots in the Fast Fourier Transform pattern assigned to the Fd-3m space group (Figures 1c,d and S2). The observed character of the Mössbauer spectrum can be explained with two possible approaches (Figures 1e, S3a, Table S2, and Supplementary Note 5). First, similarly to the Raman spectrum, it hints at a significant crystal lattice distortion, which is considered typical of the high-entropy materials, because of the various ionic radii of cations present in the structure (the so-called lattice distortion effect). Another possible explanation is in line with the Rietveld refinement fit, suggesting the location of tin in two
different crystallographic positions: mainly in the octahedral sites, but with a small amount also in tetrahedral sites. Based on the fitted spectrum, it can be concluded that all Sn exhibits +4 oxidation state, as it is expected for the spinel-type CAMs. This is also consistent with XPS measurements (Figure S3b and Supplementary Note 5). According to the XPS data, the oxidation states of all other cations in the material are +2, except for Mn$^{3+}$. Also, based on the fitted O 1s spectrum, it can be stated that the content of oxygen vacancies (at least on the surface) is rather negligible, contrary to some of the other high-entropy spinels.

Additionally, we conducted synchrotron-based XAS measurements. X-ray absorption near-edge structure (XANES) spectra for the Mg K-edge and Mn, Co, Ni, Zn L$^{3-}$-, and L$^{2-}$-edges collected in PFY mode are presented in Figure 1f, together with the reference spectra for single oxides. For Mn, the spectrum characterized with two features at 639 eV (L$_{2}$-edge) and 650 eV (L$_{2}$-edge) is in good agreement with reference Mn$_{3}$O$_{4}$ one, indicating that the Mn oxidation state is mixed $+2/+3$. For Co, features at 778 and 793 eV correspond to Co L$_{3}$- and L$_{2}$- edges. The first feature is split into two smaller peaks (779.3 and 779.9 eV), which is in good agreement with the CoO reference. However, the presence of an asymmetrical shoulder toward higher energies most probably indicates the existence of a mixed valency $+2/+3$, but with a predominant amount of Co$^{2+}$. The L$_{3}$- and L$_{2}$- edges of Ni for the pristine sample occur at energy 872.7 and 869.8 eV. Both peaks are split into two smaller ones, indicating the presence of Ni$^{2+}$. The measured L$_{3}$ edge of Zn corresponds well to the referenced ZnO. In the case of the Mg K-edge, the spectrum is similar to that of the referenced MgO, indicating +2 oxidation state. The differences between Co and Mn oxidation states from XAS results compared with XPS data (where only Co$^{2+}$ and Mn$^{3+}$ were detected) likely originate from the tendency of Mn to oxidize on the sample’s surface (XAS measured in PFY mode provides bulk information), and minor content of Co$^{3+}$ in the sample (better sensitivity of XAS). Nevertheless, based on the results from both methods, it can be stated that manganese is the cation responsible for...
charge compensation resulting from the tin deficiency. The observed tendency of Mn to exhibit a higher oxidation state can be correlated with precipitation of SnO$_2$ in the Sn1-ME5 sample and a lack of such impurity in the Sn0.8-ME5 material. The performed EDS chemical analysis (Figure S4, Table S3, and Supplementary Note 6) indicates that the obtained composition of the Sn0.8-ME5 is close to the nominal. The homogeneous distribution of the elements in the material was confirmed through the EDS mappings performed at the nanoscale (STEM, Figure 1g) and the microscale (SEM, Figure 1h). To summarize, our results unambiguously show that the nonequimolar spinel-structured HEO with a high amount of Sn (compared to the content of other cations) and a significant cation mixing can be obtained using a facile, easily scalable solid-state route.

3.2. Electrochemistry. For typical spinel-type CAM electrode materials, the initial structure is fully converted after the first lithiation and not restored during the subsequent cycles. To investigate the influence of the high-entropy spinel structure of the Sn0.8-ME5 oxide on the electrochemical properties, the material was tested in half-cells using the GDC method (Figure 2a) and compared with a pristine mixture of respective oxides (precursor after ball milling, Figure S5a). While a high initial loss of lithium, typical of conversion and alloying anodes, can be observed for both electrodes (initial coulombic efficiency: ICE$_{\text{HEO}}$ = 59%, ICE$_{\text{precursor}}$ = 63%), the
character of the curves is markedly different. Multiple voltage plateaus are visible for the precursor, originating from the electrochemical reactions of each of the constituent oxides. The curves are much more smooth for the HEO, indicating a changed lithiation mechanism. The differences between electrodes are even more pronounced in the CV curves, with the three initial cycles presented in Figure 2b for the HEO and Figure S5b for the mixture of oxides.

In the case of the precursor, as can be expected for the multiphase electrode, there are numerous peaks, also present in the subsequent scans. There is a clear drop in the peak current values between cycles, suggesting poor reversibility. Regarding the HEO, during the first lithiation, the main peak centered at ca. 0.5 V is visible, corresponding to the decomposition of the spinel structure and the formation of the solid-electrolyte interphase (SEI) film.

Figure 4. Ex situ studies of Sn0.8-MES: (a) XANES spectra the Mg K-edge and Mn, Co, Ni, Zn L\text{3}\text{-} and L\text{2}\text{-}edges measured in PFY mode for pristine, fully delithiated, and fully lithiated after 1\textsuperscript{st} and 20\textsuperscript{th} cycles electrodes, with reference spectra for simple oxides from the literature.

(b) Room-temperature \textsuperscript{119}Sn Mössbauer spectra fitted assuming two quadrupole doublets with the calculated parameters presented in Table S4 and difference spectrum at the top for fully lithiated and delithiated samples.

(c) Ex situ TEM analysis for the fully lithiated electrode: bright-field TEM images with corresponding HR-TEM analysis and FTT patterns of the whole image, showing amorphous character of the sample (left-hand side) and a mixture of amorphous phase with rock salt-like features (right-hand side, zoomed HR-TEM image); Also, the STEM/EDS map is presented, confirming maintained homogeneity of elemental distribution of the lithiated electrode.

(d) Ex situ TEM analysis for the fully delithiated electrode: bright-field TEM images with corresponding HR-TEM analysis and FTT patterns of the whole image, showing a mixture of rock salt (Fm-3m) and amorphous phases (left-hand side) and spinel-structured (Fd-3m) nanocrystallites (right-hand side). The STEM/EDS map shows that the homogeneity is still preserved upon delithiation.
the precursor indicates a more kinetically stable SEI.\textsuperscript{51} The increase of a specific current at voltages below ca. 0.45 V can be related to the ongoing alloying reaction.\textsuperscript{9} Subsequent anodic and cathodic scans are well overlapped, indicating good reversibility. The observed CV peaks can be generally divided into two main redox pairs, with peaks centered at ca. 0.02/0.55 V (lower potentials, suggesting (de-)alloying reaction\textsuperscript{10}) and ca. 0.82/1.65 V (higher potentials, suggesting conversion reaction\textsuperscript{10a}). It should be underlined that the recorded CV peaks are very broad, suggesting that both reactions are occurring gradually in a wide potential range. Such a phenomenon is an effect of the excellent mixing of active elements at the atomic scale,\textsuperscript{10a} originating from the initial random distribution of cations in the spinel phase, which is apparently also maintained during cycling. Taking into consideration that the precursor is a multiephase material with the majority of phases other than spinel (hence the effective charge transfer may be different in relation to the spinel-type HEO), it is worth comparing the reaction capacities are higher for both the precursor and SnZn intermetallics, which is apparently also maintained during cycling. For this purpose, we have employed operando XRD measurement. We found that typically inactive Mg\textsuperscript{2+} also takes part in the initial conversion reaction of the HEO, eventually giving a mixture of Mg\textsuperscript{0/2+}, with a predominant amount of the metallic state. Further emphasize that the electrochemical reaction mechanism is significantly altered for the HEO.

The altered electrochemical behavior of the Sn0.8-MES5-based electrode, compared with the studied precursor, as well as with the conventional CAMs (without electrocatalytic additives like graphene oxide, please see refs.\textsuperscript{7,8,53–56} and our experimental data for SnZn\textsubscript{O},\textsubscript{3}) requires a detailed explanation. For this purpose, we have employed operando XRD (Figure 3a,b) and EIS (Figure 3c,d) methods. We found that the spinel structure is progressively decomposing with the lithiation (decrease of the intensity of XRD peaks). The most prominent structural changes occur at around 50% of the first discharge normalized capacity (between points 4 and 5 in Figure 3c), indicating that the long plateau corresponds to the spinel decomposition and formation of the amorphous and/or nanocrystalline structure. No further changes were observed in the XRD patterns, meaning that the well-crystallized phases are not rebuilt at any stage of (de-)lithiation. Reasons for the incomplete conversion in this experiment (low-intensity Fd-3m phase peaks remain after full lithiation) are explained in Figure S6 and Supplementary Note 7. More information about properties of the electrode can be extracted from operando EIS measurements analyzed using the distribution of relaxation times (DRT) technique.\textsuperscript{58} The results are presented in Figure 3d, where the integral area of each peak is connected with the polarization resistance of a given process.\textsuperscript{57} The raw EIS data as well as the assignment of the observed peaks to the various polarization effects, together with their interpretation, are discussed in Figure S7 and Supplementary Note 8, while the DRT methodology is described in Section 2.5. Here, we focus on the qualitative change of peaks assigned to the charge transfer polarization (P\textsubscript{CT}), mainly related to the properties of studied active material.\textsuperscript{57,58} In the conversion reaction process, the charge transfer (CT) resistance is gradually decreasing (points 1–8 on the normalized curve in Figure 3c), which hints conversion of constituents of the HEO to a metallic state. The most significant modification in the P\textsubscript{CT} region occurs between points 1 and 2, indicating a substantial change of the physicochemical properties of the Sn0.8-MES,\textsuperscript{58} even at the beginning of lithiation (connected with the decomposition of the spinel observed via operando XRD measurement). Also, P\textsubscript{CT} is slightly shifted toward lower frequencies, indicating slower kinetics of CT upon lithiation. During the initial stages of delithiation, P\textsubscript{CT} is centered at higher frequencies, and the resistance further drops in the low-voltage range (points 9 and 10), suggesting that dealloying of the metals improves the transport properties. Then, the CT resistance significantly increases between points 10 and 11, reaching the highest value at the end of charge (point 12). It can be explained by the oxidation of species at higher potentials vs. Li\textsuperscript{+}/Li\textsuperscript{−}, as oxides are generally poor conductors compared with metals. Consequently, DRT results support the electrochemical character of the Sn0.8-MES5 electrode suggested by the GDC and CV measurements.

To get a deeper insight into the electrochemical mechanisms, we performed ex situ measurements at different stages of (de-)lithiation using XAS (Figure 4a), Mössbauer spectroscopy (Figure 4b), and TEM/STEM/EDS (Figure 4c,d). The detailed methodology behind the interpretation of XAS and Mössbauer spectra is described in Supplementary Note 9, while here we present only the derived conclusions. To recall, spectroscopic data indicate that Sn is at +4 state, and all the other elements of the pristine HEO material are at +2 oxidation state, except for Co\textsuperscript{2+/3+} and Mn\textsuperscript{2+/3+}. Of importance, for the fully lithiated state, surprisingly, only ca. 29% of Sn is reduced to the metallic state, while the rest remains at +4, contrary to the conventional tin-containing oxide anodes, where typically all the Sn is reduced.\textsuperscript{7,8,55} Also, the values of hyperfine parameters for Sn\textsubscript{0}, derived from Mössbauer spectra fit (Table S4 and Supplementary Note 9), suggest that highly lithiated Li–Sn intermetalics are not formed.\textsuperscript{58} Regarding Co and Ni ions, they are almost entirely reduced in the conversion reaction, with only a weak signal suggesting residue of higher oxidation states. The same can be stated for Mn; however, it becomes fully activated after 20 cycles. Zn is also found in reduced form at the end of the discharge. Unexpectedly, we found that typically inactive Mg\textsuperscript{2+} also takes part in the initial conversion reaction of the HEO, eventually giving a mixture of Mg\textsuperscript{0/2+}, with a predominant amount of the metallic state. While this phenomenon was previously inferred for (Co\textsubscript{0.4}Cu\textsubscript{0.6}Mg\textsubscript{6}Ni\textsubscript{0.2}Zn\textsubscript{0.2})O HEO,\textsuperscript{21} here it is directly evidenced for the first time. The XAS spectra measured at the intermediate lithiation states during the first cycle (Figure S8 and Supplementary Note 9) clearly show that the reduction of all the ions occurs progressively, except for Mg, which is not reduced until the end of the discharge. Therefore, in order to activate Mg\textsuperscript{2+}, other ions must first form metallic particles, which then catalyze the reaction of Mg, similarly as proposed for (Co\textsubscript{0.4}Cu\textsubscript{0.6}Mg\textsubscript{6}Ni\textsubscript{0.2}Zn\textsubscript{0.2})O.\textsuperscript{51}

As directly evidenced by the ex situ TEM studies (Figures 4c and S9a), the active material undergoes almost full amorphization upon lithiation. We detected only a minor amount of crystallites in the lithiated state, which was
identified as a spinel-structured phase (Figure S9b) with some trace of a rock salt-type phase (Figure 4c right-hand side, zoomed HR-TEM image, Figure S9a,c,d). For the latter one, the measured d-spacings match well the MgO phase (Fm-3m space group; the observation is in line with the partial presence of Mg$_{2+}$ visible in the XAS spectrum for the fully lithiated electrode). Also, a trace signal of Li$_2$O, which is expected to be a mostly amorphous product of the conversion reaction, can be found in the SAED pattern (Figure S9d). Moreover, the electrode was found to be highly homogeneous, within the spatial resolution of STEM/EDS mapping.

For the fully delithiated material, the proportion between Sn$_{0/4+}$ is the same as for the lithiated one (ca. 1:2), meaning that Sn participates only in the (de-)alloying process. Zn and...
Mn were found to work reversibly, returning to their original oxidation states. Interestingly, Co and Ni exhibit only a slight tendency for oxidation upon delithiation, yielding a limited reversible activity (likewise, this was observed for the (CoO1.25Cu0.25Mg0.25Ni0.5Zn0.25)O anode\textsuperscript{21}). Partially, Mg is oxidized back to $+2$ state, which is also clearly visible through TEM imaging (Figure 4d left-hand side, zoomed HR-TEM image, Figure S10a,b), showing exsolution of the rock salt-type MgO from the amorphous matrix. The origin of the existence of Mg\textsuperscript{2+} in the fully delithiated electrode is not understood yet, and therefore, it requires further studies. After 20 cycles at the fully lithiated state, there is even more Mg\textsuperscript{2+} than Mg\textsuperscript{0}, as compared to the fully delithiated electrode after the first cycle, leaving inactive MgO phases. However, the clearly changing proportion between 0 and +2 states during battery work indicates that this redox pair is electrochemically active. Similarly as for the lithiated material, we found nanocrystallites of a spinel-structured oxide in the delithiated material, being the electrochemically inactive part of the electrode (Figure 4d right-hand side, Figure S10c). The rest of the active material remains amorphous. Notably, the segregation of elements upon delithiation was not detected (STEM/EDS maps), meaning that nanocrystalline MgO is distributed homogeneously within the electrode.

The presented above results indicate the presence of numerous unique features related to the reversible (de-)lithiation of the Sn0.8-ME5 HEO anode. In the next section, we present a model explaining this behavior, as well as an outlook for the high-entropy anode materials in the Li-ion technology.

4. DISCUSSION AND OUTLOOK

The complex electrochemical working mechanism of the Sn-rich Sn0.8-ME5 HEO anode can be described as follows. After the first lithiation, the formed homogeneous and amorphous multicomponent matrix can be reversibly (de-)lithiated at lower potentials (alloying-type reaction) and partially, but also reversibly, oxidized at higher potentials (conversion-like reaction). Both reactions contribute to lithium storage. Because the reversible electrochemical activity of the amorphous matrix has never been observed in conventional CAMs,\textsuperscript{7,8} we believe it is the most important finding reported here, as the amorphization is known to be beneficial regarding cyclability of the anode materials.\textsuperscript{62,63} Consequently, highly lithiated crystalline intermetalics (e.g., from the Li–Sn system), characterized by significant volume changes on cycling,\textsuperscript{64} are not formed. We postulate that this change of the electrochemical reaction mechanism is due to the presence of well-mixed cations, originating from the initial structure introduced by the high-entropy approach. The role of the high entropy is therefore rather limited to ensuring the atomic-scale mixing of the elements. At the same time, it is generally considered that an electrochemically driven solid-state amorphization can be caused by the accumulation of dislocations. They can be formed upon lithiation because of the emerging electrochemical stresses, and this gives the necessary energy surplus to go far from equilibrium and create the amorphous matrix.\textsuperscript{65} This accumulation can be significantly facilitated in the high-entropy materials.\textsuperscript{66–69} It appears similar to the solid-solution strengthening effect, due to the high disorder and significant lattice distortion, both of which could be detected for the Sn0.8-ME5 HEO. On the other hand, the once formed matrix remains amorphous upon delithiation, as there are no (clearly defined) grain boundaries,\textsuperscript{70} where the crystallization occurs effectively. Moreover, working against the demixing of the disordered matrix characterized by a high structural distortion and stresses is energetically unfavorable. The crystallization can be also suppressed by kinetical limitations and the energy barriers associated with the strongly varied nearest neighbor surrounding of the cations. As evidenced in this work, there is only a gradual bulk (de-)lithiation of the multicomponent amorphous matrix ongoing. This explains why no separate electrochemical reactions are observed at potentials characteristic of each individual element of the HEO. Additionally, a minority of the inactive nanocrystalline phases is also exsolved from the amorphous matrix (rock salt and spinel). Those phases additionally buffer the volume changes.\textsuperscript{70–72} All the discussed atomic-scale effects, while resulting in the somewhat lowered capacity due to the lower level of lithiation, contribute greatly to the enhanced cycling stability. Consequently, the whole electrochemical behavior can be described in detail, without referring to the undefined “high-entropy stabilization effects.” This answers the question from the abstract about how the multicomponent solid-solution material enables reaching excellent long-term stability during cycling.

As proof of concept, we have optimized our electrode in terms of the type of binder and electrolyte additives. As visible in Figure 5a, the solid-state synthesized Sn0.8-ME5 micro-grained active material (average primary grain size equal to ca. 2 μm, Figure S4c and Supplementary Note 6) delivers a high average reversible capacity of 450 mAh g\textsuperscript{-1} under 200 mA g\textsuperscript{-1} specific current. The GDC curves between 50 and 500 cycles are well overlapped, indicating excellent reversibility (Figure 5b). Up to 200 cycles, the average discharge capacity drop per cycle is equal only to 0.24 mAh g\textsuperscript{-1} (excluding the first cycle), with an excellent capacity retention of 99.7% (comparing 200th and 30th cycles). Moreover, as visible in the ex situ SEM studies for the electrode after 200 cycles (Figures 5c,d and S11), there are virtually no morphological changes, micro-cracks, and elemental segregation visible after cycling. Importantly, the observed grains of the active HEO material are amorphous, as there is no signal from large crystalline phases detected through other techniques (except for the nanosized regions). Above around 200 cycles, the capacity starts to slightly increase with further cycling. This effect is typical of anodes with large particles involving the conversion-type reaction and is likely related to activation processes.\textsuperscript{15,24} It may also be caused by the “quasi-reversible” formation of the SEI with the continuous electrolyte decomposition, as the pronounced capacity increase occurs mainly in very low and very high potential regions\textsuperscript{89} (Figure 5b). This phenomenon has been previously observed for other spinel-type CAMs as well.\textsuperscript{71} Considering the capacity retention of the Sn0.8-ME5-based electrode in the full cycled range (comparing 500th and 2nd cycles), it reaches a value as high as 100%. The material also exhibits great stability in the rate capability test (Figure 5e), with almost fully recovered capacity after returning to the lowest current (capacity retention equal to 97%, comparing 52nd and 2nd cycles). It is worth mentioning that performance under higher currents of the studied electrode can be further improved by changing the ratio of active material to carbon additive\textsuperscript{11} to binder from 70:20:10 to 65:25:10. The long-term stability test for 900 cycles at a specific current of 500 mA g\textsuperscript{-1} is presented in Figure 5f, with the corresponding GDC curves shown in Figure S12a. While similarly as for the 70:20:10
Figure 6. Schematic of the proposed Li-storage mechanism for the Sn0.8-ME5 conversion-alloying anode material. The initially disordered and distorted high-entropy spinel lattice decomposes during the first lithiation with a concurrent SEI film formation. In this process, the lithiated homogeneous multicomponent amorphous matrix, containing Sn$^{4+}$, O$^{2-}$, Co$^{3+}$, Mg$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$, is created. Mg$^{2+}$ is partially reduced to Mg$^{0}$. There is a small amount of residual electrochemically inactive nanocrystalline phases: MgO (rock salt) and spinel. Amorphous-like Li$_{x}$O is formed as well. The fully lithiated matrix contains a significant amount of Sn in the oxidized (+4) state, together with some amount of oxygen ions. The main amorphous matrix is reversibly (de-)lithiated through both the alloying-like reaction (low potentials) and conversion-like reaction (higher potentials). Only Zn and Mn undergo fully reversible conversion (between 0 and $+2$ states), delivering ca. 30% of the capacity. The remaining 70% of the capacity is ascribed to the alloying-like reaction of the amorphous matrix. Upon delithiation, the recrystallization does not occur, as working against demixing of the disordered matrix is energetically unfavorable, and there are no grain boundaries for a facile crystallization.

electrode the increase of capacity for prolonged cycling can be observed, this result further proves the great cyclability of the developed HEO, even for higher rates. The influence of the optimized carbon content on the accessible reversible capacity at a specific current of 200 mA g$^{-1}$ for 200 cycles is presented in Figures S12b,c. In the case of the carbon content-optimized electrode, the observed average discharge capacities in the entire cycled range are outstanding and equal to 569 mAh g$^{-1}$ for 200 mA g$^{-1}$ and 438 mAh g$^{-1}$ for 500 mA g$^{-1}$. Additionally, to investigate the performance at even higher currents, for the cell cycled initially 750 times at 500 mA g$^{-1}$, additional tests were conducted, comprising 50 cycles at 1000 mA g$^{-1}$, followed by 50 cycles at 2000 mA g$^{-1}$. The obtained, stabilized capacities were ca. 280 and 165 mAh g$^{-1}$, respectively. In general, to our knowledge, this is so far the best ever observed cyclability for the solid-state synthesized CAMs$^{8,9}$ proving that the high-entropy approach can be successfully applied for preparing anodes using facile and low-cost synthesis routes, instead of going toward sophisticated and complex synthesis methods.$^{72}$

The proposed Li-storage mechanism for Sn0.8-ME5 HEO is schematically summarized in Figure 6. Additionally, the capacity for the first lithiation and the reversible capacity were compared with the calculated theoretical capacities (taking into consideration the experimental capacity from the rate capability test under a low specific current of 50 mA g$^{-1}$, Supplementary Note 10). As discussed above, only Zn and Mn ions, embedded in the amorphous matrix, can undergo fully reversible conversion reactions. This corresponds to ca. 30% of the reversible capacity. The remaining 70% of the capacity must originate from the reversible alloying-like reaction of the amorphous matrix, that is occurring without a change of the oxidation state of any particular element, but rather through electron exchange within the entire homogeneous matrix. Also, the observed capacity is significantly lower when compared with the theoretical capacity of the HEO system, considering all the possible conventional reactions (Supplementary Note 10). This underlines the fact that the Li-storage mechanism is indeed significantly changed for the Sn0.8-ME5, as well as that the excellent long-term stability of the HEO related to the altered (de-)lithiation mechanism results in lowered capacity.

Based on our results, guidelines for the future development of HEO-based anodes can be provided. Further studies of the Sn-rich conversion-alloying HEOS should focus on the optimization of the chemical composition, for which the high-entropy approach provides vast possibilities. In particular, this optimization should aim to improve performance by increasing the amount of the alloying-based elements per mole of HEO (nonequimolar approach), which also seems to be a good direction for the development of the conventional CAMs.$^{90}$ In the light of our results, HEOS do not necessarily need to be equimolar to achieve excellent cycling stability in Li-ion cells, as long as multiple main elements, characterized by various physicochemical properties, are well-mixed within the initial structure. Therefore, we believe that the maximization of the configurational entropy is in fact not crucial here.

In summary, the presented approach of designing a high-entropy conversion-alloying anode material shall contribute to the improvement of the performance of Li-ion batteries. It allows achieving excellent long-term stability of the anode material manufactured using a simple solid-state reaction route. It also provides great opportunities for further optimization, for
example, by increasing the amount of the elements undergoing alloying reaction, which shall lead to the increased energy density of the cells (because of the higher capacity and lower operation voltage of the anode material).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c11038.

Literature description about CAMs and HEOs; description of the selection of the system; XRD analysis with XRD patterns for Sn1-ME5 and Sn0.8-ME5 compositions and electrochemical performance of Sn1-ME5; TEM and SAED analysis of the pristine Sn0.8-ME5; Raman, Mössbauer, and XPS analysis together with corresponding spectra for pristine Sn0.8-ME5; studies of morphology and chemical composition of Sn0.8-ME5 powder via SEM, TEM, EDS, and DLS methods; electrochemical properties of the precursor for HEO synthesis; ex situ XRD patterns compared with operando XRD measurement; operando EIS with DRT analysis and presentation of the raw EIS spectra; analysis of the ex situ Mössbauer spectroscopy data; analysis of the ex situ XAS data with measured spectra for partially lithiated Sn0.8-ME5-based electrodes; complementary ex situ TEM results for both lithiated and delithiated Sn0.8-ME5-based electrodes; ex situ SEM analysis results together with EDS maps for the optimized electrode (pristine and after 200 cycles); cycling performance for the Sn0.8-ME5-based electrode with different active material to carbon ratios; and calculation of the theoretical capacity of the Sn0.8-ME5 anode material (PDF)

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**Notes**

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**REFERENCES**

(1) Sun, Y.; Liu, N.; Cui, Y. Promises and Challenges of Nanomaterials for Lithium-Based Rechargeable Batteries. Nat. Energy 2016, 1, 16071.

(2) Chu, S.; Cui, Y.; Liu, N. The Path towards Sustainable Energy. Nat. Mater. 2016, 16, 16–22.

(3) Mahmood, N.; Tang, T.; Hou, Y. Nanostructured Anode Materials for Lithium Ion Batteries: Progress, Challenge and Perspective. Adv. Energy Mater. 2016, 6, No. 1600374.

(4) Eshetu, G. G.; Zhang, H.; Jüdes, X.; Adenusi, H.; Armand, M.; Passerini, S.; Figgemeier, E. Production of High-Energy Li-Ion Batteries Comprising Silicon-Containing Anodes and Insertion-Type Cathodes. Nat. Commun. 2021, 12, 5459.

(5) Andersen, H. F.; Foss, C. E. L.; Voje, J.; Tronstad, R.; Mokkelbost, T.; Vullum, P. E.; Ulvestad, A.; Kirkengen, M.; Mæhlen, M.; P-hansen, K.; Madsen, J. P. Silicon-Carbon Composite Anodes from Industrial Battery Grade Silicon. Sci. Rep. 2019, 9, 14814.

(6) Li, P.; Kim, H.; Myung, S. T.; Sun, Y. K. Diverting Exploration of Silicon Anode into Practical Way: A Review Focused on Silicon-Graphite Composite for Lithium Ion Batteries. Energy Storage Mater. 2021, 35, 550–576.

(7) Bresser, D.; Passerini, S.; Scrosati, B. Leveraging Valuable Synergies by Combining Alloying and Conversion for Lithium-Ion Anodes. Energy Environ. Sci. 2016, 9, 3348–3367.
(8) Reddy, M. V.; Subba Rao, G. V.; Chowdari, B. V. R. Metal Oxides and Oysalts as Anode Materials for Li Ion Batteries. Chem. Rev. 2013, 113, 5364–5457.

(9) Obrovac, M. N.; Chevrier, V. L. Alloy Negative Electrodes for Li-Ion Batteries. Chem. Rev. 2014, 114, 11444–11502.

(10) Cao, K.; Jin, T.; Yang, L.; Jiao, L. Recent Progress in Conversion Reaction Metal Oxide Anodes for Li-Ion Batteries. Mater. Chem. Front. 2017, 1, 2213–2242.

(11) Wang, H. Y.; Wang, B. Y.; Meng, J. K.; Wang, J. G.; Jiang, Q. C. One-Step Synthesis of Co-Doped ZnSnO$_4$-Graphene-Carbon Nanocomposites with Improved Lithium Storage Performances. J. Mater. Chem. A 2014, 3, 1023–1030.

(12) Lun, Z.; Ouyang, B.; Kwon, D. H.; Ha, Y.; Foley, E. E.; Huang, T. Y.; Cai, Z.; Kim, H.; Balasubramanian, M.; Sun, Y.; Huang, J.; Tian, Y.; Kim, H.; McClosey, B. D.; Yang, W.; Clément, R. J.; Ji, H.; Ceder, G. Cation-Disordered Rocksalt-Type High-Entropy Cathodes for Li-Ion Batteries. Nat. Mater. 2020, 20, 211–219.

(13) Wang, Q.; Sarkar, A.; Wang, D.; Velasco, L.; Azmi, R.; Bhattacharya, S. S.; Bergfeldt, T.; Dıveı, A.; Heitjans, P.; Brezesinski, T.; Hahn, H.; Breitung, B. Multi-Anionic and -Cationic Compounds: New High Entropy Materials for Advanced Li-Ion Batteries. Energy Environ. Sci. 2019, 12, 2433–2442.

(14) Wang, J.; Cui, Y.; Wang, Q.; Wang, K.; Huang, X.; Stenzel, D.; Sarkar, A.; Azmi, R.; Bergfeldt, T.; Bhattacharya, S. S.; Kruk, R.; Hahn, H.; Schweidler, S.; Brezesinski, T.; Breitung, B. Lithium Containing Layered High Entropy Oxide Structures. Sci. Rep. 2020, 10, 18430.

(15) Sarkar, A.; Velasco, L.; Wang, D.; Wang, Q.; Talasila, G.; de Biasi, L.; Kübel, C.; Brezesinski, T.; Bhattacharya, S. S.; Hahn, H.; Breitung, B. High Entropy Oxides for Reversible Energy Storage. Nat. Commun. 2018, 9, 3400.

(16) Wang, Q.; Sarkar, A.; Li, Z.; Lu, Y.; Velasco, L.; Bhattacharya, S. S.; Brezesinski, T.; Hahn, H.; Breitung, B. High Entropy Oxides as Anode Material for Li-Ion Battery Applications: A Practical Approach. Electrochem. Commun. 2019, 100, 121–125.

(17) Chen, H.; Qiu, N.; Wu, B.; Yang, Z.; Sun, S.; Wang, Y. Tunable Pseudocapacitive Contribution by Dimension Control in Nano-crystalline-Constructed (Mg$_{0.2}$Co$_{0.2}$Cu$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)O Solid Solutions to Achieve Superior Lithium-Storage Properties. RSC Adv. 2019, 9, 28098–28105.

(18) Kheradmandfard, M.; Minouei, H.; Tsvetkov, N.; Vayghan, A. K.; Kashani-Bozorg, S. F.; Kim, G.; Hong, S. I.; Kim, D. E. Ultrafast Green Microwave-Assisted Synthesis of High Entropy Oxide Nanoparticles for Li-Ion Battery Applications. Mater. Chem. Phys. 2021, 262, No. 124265.

(19) Wang, J.; Stenzel, D.; Azmi, R.; Najib, S.; Wang, K.; Jeong, J.; Sarkar, A.; Wang, Q.; Sukkurji, P. A.; Bergfeldt, T.; Botros, M.; Mailbach, J.; Hahn, H.; Brezesinski, T.; Breitung, B. Spinel to Rock-Salt Transformation in High Entropy Oxides with Li Incorporation. Adv. Mater. Interfaces 2019, 6, No. 156158.

(20) Nguyen, T. X.; Patra, J.; Chang, J. K.; Jing, T. M.; Chang, J. K. Effects of Elemental Modulation on Phase Purity and Electrochemical Performances of (Co$_{0.2}$Co$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)O with Superior Lithium-Storage Performance. J. Mater. Chem. A 2018, 6, 11502–11507.

(21) Chen, H.; Qiu, N.; Wu, B.; Yang, Z.; Sun, S.; Wang, Y. New Spinel High-Entropy Oxides (FeCoNiCrMn)$_{0.2}$O with Fast Reaction Kinetics and Excellent Stability as an Anode Material for Li-Ion Batteries. RSC Adv. 2020, 10, 9736–9744.

(22) Yang, D.; Jiang, S.; Duan, C.; Mao, J.; Dong, Y.; Song, J.; Wang, Z.; Luo, S.; Liu, Y.; Qi, X. Spinel-Structured High Entropy Oxide (FeCoNiCrMn)$_{0.2}$O as Anode towards Superior Lithium Storage Performance. J. Alloys Compd. 2020, 844, No. 156158.

(23) Chen, H.; Jiang, J.; Sun, S.; Wang, Y. New High-Entropy Oxides (MgCoNiZn)$_{0.2}$Li$_{0.2}$O as Anode Material for Lithium-Ion Batteries. ACS Appl. Mater. Interfaces 2020, 12, 23860–23866.

(24) Chen, T.-Y.; Wang, S.-Y.; Kuo, C.-H.; Huang, S.-C.; Lin, M.-H.; Li, C.-H.; Chen, H.-Y. T.; Wang, C.-C.; Liao, Y.-F.; Lin, C.-C.; Chang, Y.-M.; Yeh, J.-W.; Lin, S.-J.; Chen, T.-Y.; Chen, H.-Y. In Operando Synchrotron X-Ray Studies of a Novel Spinel (Ni$_{0.2}$Co$_{0.2}$Mn$_{0.2}$Fe$_{2}$O$_{3}$)O High-Entropy Oxide for Energy Storage Applications. J. Mater. Chem. A 2020, 8, 21756–21770.

(25) Kocık, E.; Toparlı, Ç.; Anıl, K. Electrochemical Performance of (MgCoNiZn)$_{0.2}$Li$_{0.2}$O High-Entropy Oxides in Lithium-Ion Batteries. ACS Appl. Mater. Interfaces 2020, 12, 23860–23866.
[51] Ma, Q.; Wu, S.; Fan, Y. Synthesis and Microwave Dielectric Properties of Zn2SnO4 Ceramics. *Ceram. Int.*, 2014, 40, 1073–1080.

(52) Madern, N.; Monnier, J.; Baudourd-Hejadian, R.; Steckmeyer, A.; Joubert, J. M. Characterization of Refractory Steel Oxidation at High Temperature. *Corros. Sci.* 2018, 132, 223–233.

(53) Cheng, B.; Lou, H.; Sarkar, A.; Zeng, Z.; Zhang, P.; Chen, X.; Tan, L.; Prakapenka, V.; Greenberg, E.; Wen, J.; Djenicad, R.; Hahn, H.; Zeng, Q. Pressure-Induced Tuning of Lattice Distortion in a High-Entropy Oxide. *Commun. Chem.* 2019, 2, 114.

(54) Wang, B.; Yao, J.; Wang, J.; Chang, A. Spinel-Type High-Entropy (Co0.2Mn0.2Fe0.2Zn0.2Ti0.2)O3 Oxides Constructed from Disordered Cations and Oxygen Vacancies. *J. Alloys Compd.* 2022, 897, 161188.

(55) Zhao, J.; Yang, X.; Huang, Y.; Du, F.; Zeng, Y. Entropy Stabilization Effect and Oxygen Vacancies Enabling Spinel Oxide Highly Reversible Lithium-Ion Storage. *ACS Appl. Mater. Interfaces* 2021, 13, 58674–58681.

(56) Gilbert, B.; Frazer, B. H.; Belz, A.; Conrad, P. G.; Nealon, K. H.; Haskel, D.; Lang, J. C.; Srajer, G.; De Stasio, G. Multiple Scattering Calculations of Bonding and X-Ray Absorption Spectroscopy of Manganese Oxides. *J. Phys. Chem. A* 2003, 107, 2839–2847.

(57) Liu, X. C.; Shi, E. W.; Chen, Z. Z.; Chen, B. Y.; Huang, W.; Song, L. X.; Zhou, K. J.; Cui, M. Q.; Xie, Z.; He, B.; Wei, S. Q. The Local Structure of Co-Doped SnO Films Studied by X-Ray Absorption Spectroscopy. *J. Alloys Compd.* 2008, 463, 435–439.

(58) Qiao, R.; Wray, L. A.; Kim, J. H.; Pieczonka, N. P. W.; Harris, S. J.; Yang, W. Direct Experimental Probe of the Ni(II)/Ni(III)/Ni(IV) Redox Evolution in LiNi0.25Co0.25Mn0.5O2. *Electrodes. J. Phys. Chem. C* 2015, 119, 27228–27233.

(59) Eisenmann, T.; Asenbauer, J.; Rezvani, S.; Ju, J.; Kwon, Y. U.; Zhao, Y. Improved Capacity and Cycling Stability of SnO2 Nanoparticles Induced by Amorphization during Cycling for Lithium Ion Batteries. *J. Power Sources* 2019, 180, No. 107973.

(60) Jiang, Y.; Song, Y.; Pan, Z.; Meng, Y.; Jiang, L.; Wu, Z.; Yang, P.; Gu, Q.; Sun, D.; Hu, L. Rapid Amorphization in Metastable CoSe2 nanostructures for ultrafast Lithiation Kinetics. *ACS Nano* 2018, 12, 5011–5020.

(61) Sen, R.; Johari, P. Understanding the Lithiation of the Sn Anode for High-Performance Li-Ion Batteries with Exploration of Novel Li-Sn Compounds at Ambient and Moderately High Pressure. *ACS Appl. Mater. Interfaces* 2017, 9, 40197–40206.

(62) Huang, J. Y.; Zhang, L.; Wang, C. M.; Sullivan, J. P.; Xu, W.; Chang, L. Q.; Mao, S. X.; Hudak, N. S.; Liu, X. H.; Subramanian, A.; Fan, H.; Qi, L.; Kushima, A.; Li, J. In Situ Observation of the Electrochemical Lithiation of a Single SnO2 Nanowire Electrode. *Science* 2010, 330, 1515–1520.

(63) Chen, H.; Kauffmann, A.; Laube, S.; Choi, I. C.; Schwager, R.; Huang, Y.; Lichtenberg, K.; Müller, F.; Gorr, B.; Christ, H. J.; Heilmann, M. Contribution of Lattice Distortion to Solid Solution Strengthening in a Series of Refractory High Entropy Alloys. *Metall. Mater. Trans. A* 2018, 49, 772–781.

(64) Zhao, S.; Li, Z.; Zhu, C.; Yang, W.; Zhang, Z.; Armstrong, D. E. J.; Grant, P. S.; Ritchie, R. O.; Meyers, M. A. Amorphization in Extreme Deformation of the CrMnFeCoNi High-Entropy Alloy. *Sci. Adv.* 2017, 3, 5011–5020.

(65) Wang, H.; Chen, D.; An, X.; Zhang, Y.; Sun, S.; Tian, Y.; Zhang, Z.; Wang, A.; Liu, J.; Song, M.; Ringer, S. P.; Zhu, T.; Liao, X. Deformation-Induced Crystalline-to-Amorphous Phase Transformation in a CrMnFeCoNi High-Entropy Alloy. *Sci. Adv.* 2021, 7, No. aeb3108.

(66) Ikeda, Y.; Gubeav, K.; Neugebauer, J.; Grabowski, B.; Körnmann, F. Chemically Induced Local Lattice Distortions versus Structural Phase Transformations in Compositionsally Complex Alloys. *npj Comput. Mater.* 2021, 7, 34.

(67) Buchholz, D. B.; Ma, Q.; Alducin, D.; Ponce, A.; Jose-Yacaman, M.; Khanal, R.; Medvedeva, J. E.; Chang, R. P. H. The Structure and Properties of Amorphous Indium Oxide. *Chem. Mater.* 2014, 26, 5401–5411.

(68) Liu, H.; Zhu, Z.; Yan, Q.; Yu, S.; He, X.; Chen, Y.; Zhang, R.; Ma, L.; Liu, T.; Li, M.; Lin, R.; Chen, Y.; Li, Y.; Xing, X.; Choi, Y.; Gao, L.; Cho, H. S.; An, K.; Feng, J.; Kostoecki, R.; Amine, K.; Wu, T.; Lu, J.; Xin, H. L.; Ong, S. P.; Liu, P. A Disordered Rock Salt Anode for Fast-Charging Lithium-Ion Batteries. *Nature* 2020, 585, 63.

(69) Akbashev, A. R. Electrocatalysis Goes Nuts. *ACS Catal.* 2022, 12, 4296–4301.