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Preface

The development of advanced materials for energy storage devices, such as batteries, supercapacitors, and dielectric capacitors is becoming increasingly important as the world's energy demands continue to rise. The broad adoption of renewable energy technologies is constantly hampered by the inherent performance, durability, and cost-effectiveness limitations of traditional materials, despite their extensive research and optimization. With the introduction of high-entropy materials (HEMs) in recent decades, a paradigm shift in materials science has started to address these issues. HEMs adopt a multi-elemental philosophy, usually incorporating five or more elements in equiatomic or near-equiatomic ratios, in contrast to the traditional method of designing materials around one or two principal elements. Increased strength, outstanding thermal stability, superior corrosion and wear resistance, and intriguing electrochemical behavior are just a few of the remarkable properties that result from this unusual compositional complexity, which also creates special synergistic effects. These properties are frequently better than those of their conventional counterparts.

This book, *High-Entropy Materials for Energy Storage Devices*, aims to provide a comprehensive and timely exploration of this exciting and rapidly evolving field. Herein, we highlights the basic concept of various high-entropy materials (especially alloy and oxides-based materials), advanced synthesis techniques, characterization, mechanism, and potential energy storage applications for the battery, dielectric capacitor, and supercapacitor. Our goal is to bridge the gap between fundamental materials science and practical energy device engineering. We seek to equip researchers, engineers, and students with a thorough understanding of how the unique attributes of high-entropy materials can be harnessed to overcome current limitations in energy storage technologies. By bringing together diverse perspectives on synthesis, characterization, theoretical modeling, and device integration, we hope to inspire further innovation and accelerate the development of next-generation energy storage solutions. We sincerely hope that this book will be a vital resource and a driving force behind future innovations, making a substantial contribution to a world that is more energy-secure and sustainable.

Dr. Chien-Te Hsieh
Dr. Pradeep Kumar Panda
Dr. Arpan Kumar Nayak

List of Abbreviations

Abbreviation	Definition
AC	Activated carbon
AI	Artificial intelligence
BCC	Body-centered cubic
CVD	Chemical vapor deposition
CV	Cyclic voltammetry
DFT	Density functional theory
EDLC	Electrical double-layer capacitance
FCC	Face-centered cubic
FSP	Flame spray pyrolysis
GITT	Galvanostatic intermittent titration technique
HEA	High-entropy alloy
HEM	High-entropy material
HEO	High-entropy oxide
HEPO	High-entropy perovskite oxide
HEPBA	High-entropy Prussian blue analogue
HE-SC-N88	$LiNi_{0.88}Mn_{0.03}Mg_{0.02}Fe_{0.02}Ti_{0.02}Mo_{0.02}Nb_{0.01}O_2$
LIB	Lithium-ion battery
ML	Machine learning
M-HEM	Metal-doped high-entropy material
MD	Molecular dynamics
PBA	Prussian blue analogue
SSB	Solid-state battery
SC	Supercapacitor
SC-NCM88	SC $LiNi_{0.88}Co_{0.09}Mn_{0.03}O_2$
SIB	Sodium-ion battery

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Overview of High-Entropy Materials for Energy Storage

Surface Chemistry and Its Functionality

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1.1 Introduction

High-entropy materials (HEMs) have emerged as a revolutionary class of materials that promises unparalleled possibilities to develop energy storage and energy conversion devices [1–3]. This class of materials is defined by the presence of multiple-principal elements in equimolar or near-equimolar compositions. HEMs are characterized by entropy-stabilized composition, which dictates the structural, phase, and electrochemical stability [4–7]. The configurational entropies of these materials drive single-phase solid solution forms, suppressing phase segregation and improving stability under aggressive electrochemical conditions [8] (see Scheme 1.1). These characteristics make HEMs of special interest to next-generation lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), and all-solid-state batteries (ASSBs) where the conventional materials are prone to limitations in performance encompassing structural degradation, capacity decay, and kinetic inefficiency.

One of the key aspects of HEMs that enables them to exhibit superior electrochemical performance is their modified compositional chemistry. Unlike energy storage materials of the past, where there are limited elements that control performance, HEMs take advantage of multi-principal element combinations to develop tunable electrochemical properties, such as increased ionic conductivity, decreased charge transfer resistance, and phase stability [9–11]. Through the strategic choice

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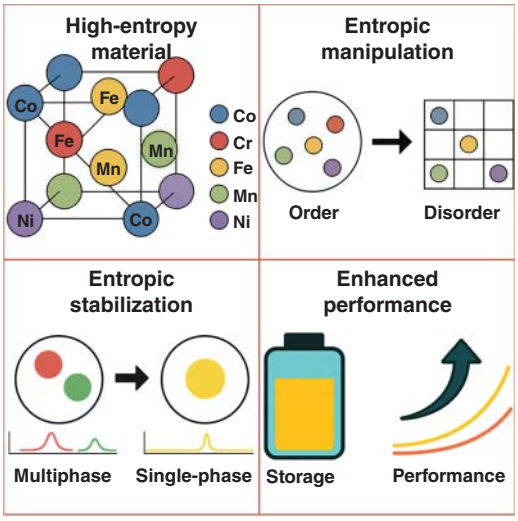

Scheme 1.1 Schematic illustration of HEMs enabling entropic disorder, phase stabilization, and enhanced electrochemical performance in energy storage for next-generation energy storage devices.

and optimization of elemental compositions, it is possible to design these materials to have low activation energies (E_a), high-power densities, and extended cycling life, making them potential materials of choice for electrodes (anode/cathode) and electrolyte (liquid/solid) in high-performance battery systems [12–15].

In this chapter, the fundamental role of compositional chemistry in determining the electrochemical properties of HEM-based energy devices is discussed. This includes the kinetic and thermodynamic fundamentals of entropy stabilization and how these affect phase transformations, structural stability, and electrochemical robustness [16–18]. The relation between multiple-elemental correlations, redox activity, and defect chemistry is discussed, detailing how each of these influences the functional characteristics of HEMs in batteries. Another key focus of this chapter is the introduction of analysis methods used to characterize phase and compositional stability within high-entropy systems. Advanced in situ methods, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and electrochemical impedance spectroscopy (EIS), yield rich information on dynamic phase transformation within HEMs under operating conditions [19–25]. These techniques are used to monitor phase transformation, defect formations, and interfacial behavior in real time, allowing the optimization of HEMs to achieve ideal electrochemical properties. The chapter also discusses case studies that demonstrate compositional engineering application to HEM-based electrolytes and electrodes. Strategic control of compositions is shown which lead to significantly improved cycling stability, rate capacity, and energy density, highlighting the real benefits of high-entropy systems in next-generation battery systems [26–28]. By combining the fundamental concepts of compositional entropy, defect thermodynamics, and surface chemistry, the chapter presents a holistic view

of the rationale-based design of HEMs for energy storage devices. The information discussed here is anticipated to chart the direction of future research in high-entropy battery materials to allow the development of high-performance, and sustainable energy storage devices.

1.2 Fundamental Principles in HEMs

1.2.1 Definition and Fundamental Principles

HEMs are a new class of materials characterized by multi-principal elements. Unlike materials based on a binary, ternary, or quaternary compositions, HEMs have five or more elements in near-equimolar or equimolar compositions, resulting in high configurational entropy [29]. The fundamental design principle of an HEM lies in the fine-tuning of configurational entropy, which measures the disorder brought into a system of a single phase by multiple elements [30, 31]. Through the entropic pathway, stable solid solutions are favored, and phase segregation is reduced, enhancing the phase stability of the material under harsh conditions.

Configurational entropy of a multicomponent system is quantified by the Boltzmann equation [3]:

$$S_{Config}^{Ideal} = -k_B \sum_{i=1}^{N} x_i \ln x_i \tag{1.1}$$

where x_i is the mole fraction of the i^{th} component, and k_b is the Boltzmann constant. For a system of N number of elements in equimolar concentration, Eq. 1.1 simplifies to:

$$S_{Config}^{Ideal} = -R \ln (N) \tag{1.2}$$

where R is the general gas constant. Empirically, a system is classified as an HEM if its configurational entropy exceeds 1.5 k_B per site. For instance, when $N = 5$, the entropy reaches approximately 1.6 k_B, which aligns with the threshold for high-entropy classification [3, 32].

Thus, the threshold criteria are as follows [3]:

- High-entropy phase: $S_{Config}^{Ideal} \geq 1.5\, k_B$
- Medium-entropy phase: $1.0\, k_B \leq S_{Config}^{Ideal} < 1.5\, k_B$
- Low-entropy phase: $S_{Config}^{Ideal} < 1.0\, k_B$

This entropic effect promotes the formation of thermodynamically stable, single-phase structures that can withstand electrochemical cycling without significant phase decomposition.

1.2.2 Classification and Types of Entropy in HEMs

While configurational entropy is a defining feature of HEMs, other entropy contributions also play critical roles in material stability and performance, including conformational entropy $\left(S_{Config}^{Ideal}\right)$ which is related to the spatial arrangement of

atoms and their degrees of freedom, vibrational entropy $\left(S_{Vib}^{Ideal}\right)$ arising from atomic lattice vibrations, influencing phase stability at different temperatures, rotational and translational entropy significantly considered in liquid-state or polymer-based multicomponent systems and cavity entropy which is associated with voids and defects in crystalline or amorphous structures.

One needs to understand that just by virtue of having a number of elements within the material does not mean that it is automatically a material of high-entropy. How the elements are distributed, what constitutes the phases, what the role of entropy is all play a cumulative role in deciding whether or not the system itself is of a high-entropy nature. Terms such as "entropy stabilization" and "compositionally complex materials (CCMs)" are often used interchangeably with HEMs but possess distinct technical meanings.

1.2.3 High-Entropy Materials in Energy Storage Systems

Incorporation of HEMs with electrolyte and electrode materials has opened new avenues for the development of energy storage technologies. They consist of severely disordered lattice structures with many internal defects, increasing the ion migration and decreasing the activation energies. These characteristics have placed the HEMs at the forefront for future battery technologies, such as high-entropy oxides (HEOs) as anode materials for LIBs, exhibiting high cycling stability and exceptional rate capabilities [33]; high-entropy sulfides (HESs) and high-entropy phosphides with fast ionic conductivity, making them promise for solid-state electrolyte (SSE) applications [34, 35]; and high-entropy alloys (HEAs) and ceramics for structural components in SIBs and Li-S batteries [3, 8].

Recent innovations in zero/low-strain cathodes and multicomponent anodes have demonstrated remarkable improvements in electrochemical stability, making HEMs highly attractive for high-rate and high-voltage applications. Additionally, their ability to replace scarce or toxic elements with earth-abundant alternatives promotes sustainability in energy storage technologies.

1.2.4 Ion Transport Mechanisms in HEMs

Liquid- and solid-state HEM preparations generally entail combinations of several salts and additives in inorganic or organic solvents [2, 3]. Productive solute–solvent interactions alter order–disorder features in favor of increasing the stability of the electrolyte and ionic transport functionality. In high-entropy liquid electrolytes (HELEs) and high-entropy solid-state electrolytes (HESEs), the presence of multiple ionic species introduces a complex network, leading to uneven energy distribution among ions and modification of Li^+ hopping site energy, enhancing ion mobility in SSEs.

The diffusion coefficient of Li^+ in such systems follows the relation:

$$D_i = ae^{\left(\frac{bS_{Config}^{Ideal}}{k_B}\right)} \tag{1.3}$$

n

o

p

t