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An Overview of Transition Metal Oxides for Electrochemical Energy Storage

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Transition metal oxides (TMOs) are used in many commercial and research applications, including catalysis, electrochemical energy storage/conversion, electronics, and thermoelectrics. This book focuses on TMOs for electrochemical energy storage devices with particular emphasis on intercalation-based secondary (rechargeable) batteries. This introductory chapter provides a broad overview of such applications, and detailed treatments of specific subjects are given in Chapters 2–16.

1.1 Fundamentals of Electrochemical Cells

An electrochemical cell consists of two electrodes (denoted as cathode/anode or positive/negative) separated by an ionically conductive, electronically insulating electrolyte. Batteries convert chemical energy into electrical energy through Faradaic charge transfer processes where: (i) oxidation/reduction reactions occur within anode/cathode active materials and (ii) electrons are transported through an external circuit to maintain charge neutrality at each electrode. These reactions are irreversible in primary batteries (e.g. Zn–MnO₂ and Li–MnO₂) designed for single-use applications. On the other hand, secondary batteries (e.g. lead-acid, nickel-metal hydride, and Li-ion) leverage reversible redox processes and can be repeatedly charged/discharged, a requirement for many end-use applications (e.g. electric vehicles).

Electrochemical capacitors are another form of energy storage devices which provide specific energy and power between that of dielectric capacitors and rechargeable batteries. Supercapacitors store/deliver energy through non-Faradaic processes where ions are stored in the electrochemical double layer near the electrode surfaces. On the other hand, pseudocapacitive materials store energy through charge transfer reactions which may include: (i) oxidation/reduction of the electrode surface and/or (ii) intercalation of ions into a host active material. Hybrid configurations utilizing pseudocapacitive materials approach the specific energy of rechargeable batteries.

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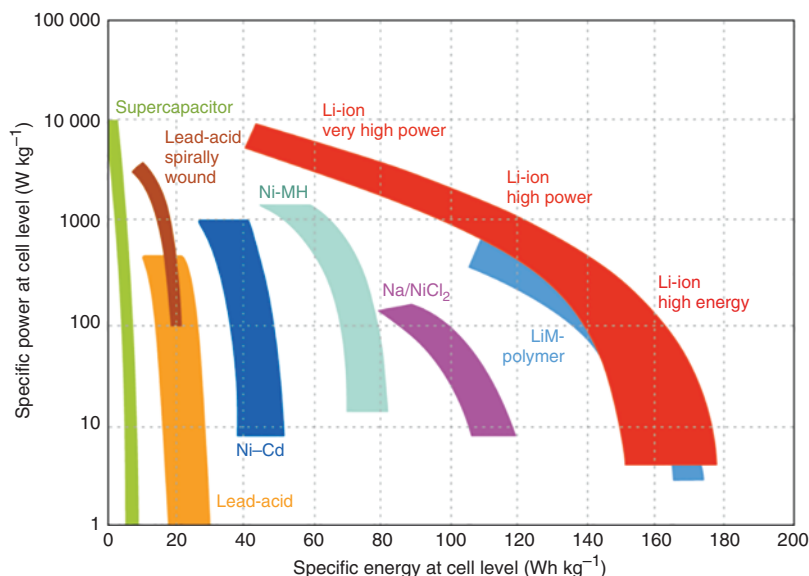


Figure 1.1 Ragone plot showing the specific energy and power of several electrochemical energy storage systems. Source: Image reproduced from Hayner et al. [1], International Energy Agency, Technology Roadmaps: Electric and Plug-in Hybrid Electric Vehicles, 2009, p. 12. (Original source: Johnson Control – SAFT 2005 and 2007.)

Two important performance metrics of energy storage devices are the specific energy (Wh kg⁻¹) and specific power (W kg⁻¹), which describe *how much* and *how quickly* energy can be stored/delivered, respectively. Analogous quantities normalized to system volume (i.e. energy/power densities with units of Wh L⁻¹ and W L⁻¹) are also commonly used. Ragone plots (Figure 1.1) summarize these energy/power relationships and are useful to assess the viability of different energy storage platforms for a given application. Figure 1.1 shows a fundamental tradeoff between a system's specific energy and power. For example, supercapacitors exhibit: (i) high specific power due to rapid ion adsorption/desorption near electrode surfaces but (ii) low specific energy since charge storage only occurs within the electrochemical double layer. On the other hand, batteries store energy within the bulk structure of active materials, enabling high specific energy. The rate of energy storage/delivery in batteries is generally limited by solid-state diffusion or phase nucleation kinetics in the active material, resulting in lower specific power than supercapacitors. With these trends in mind, it should be emphasized that the energy/power characteristics of an electrochemical device are also highly dependent on design factors such as material selection, cell format, and electrode architecture.

Sections 1.2–1.5 provide basic overviews of electrochemical energy storage devices where TMOs play critical roles in device operation. The importance of advanced characterization and computing resources on guiding material development, understanding degradation mechanisms, and optimizing system performance is also highlighted.

1.2 Li-Ion Batteries: Basic Principles and TMO Electrodes

Over the last four decades, Li-ion batteries have successfully transitioned from research and development to commercial applications, including portable electronics, electric vehicles, and grid storage. The foundation of this technology is based on cation intercalation reactions wherein Li^+ is stored in TMO cathodes and graphite anodes [2]. These intercalation reactions are highly reversible, and today's Li-ion batteries can undergo hundreds or thousands of cycles with minimal chemical and/or structural changes to the active material (see Chapters 9 and 10 for detailed discussion on degradation mechanisms of Li-ion batteries).

The working principles of Li-ion batteries are illustrated in Figure 1.2. During charge, Li^+ deintercalate from the TMO cathode (e.g. LiCoO_2), transport through the electrolyte, and intercalate into the anode active material (e.g. graphite). To maintain charge neutrality, electrons are simultaneously extracted from the cathode (typically via transition metal oxidation), transported through an external circuit, and inserted in the anode (electrochemical reduction of graphite). During discharge, these processes are reversed, and Li^+ ions and electrons are transported back to the cathode. Figure 1.2b shows qualitative cathode/anode voltage profiles as a function of capacity. Commercial Li-ion batteries typically have cell voltages ~ 3.6 V and specific energies ~ 200 Wh kg^{-1} , although these values depend on active material selection and cell design.

Commercial Li-ion electrodes are prepared by casting a slurry containing active material (the host material which reversibly stores Li^+), electronically conductive carbon additives, and polymer binder onto a current collector (typically Cu for the anode and Al for the cathode). Key electrochemical properties, including operating voltage, reversible capacity, and cyclability, are strongly dependent on the active material's crystallographic structure and transition metal selection. Conventional cathode active materials include: (i) lithium TMOs with layered or spinel crystallographic structures (e.g. LiCoO_2 and LiMn_2O_4 , respectively) and (ii) olivine structures containing polyanionic groups (e.g. LiFePO_4). A wide range of related compositions

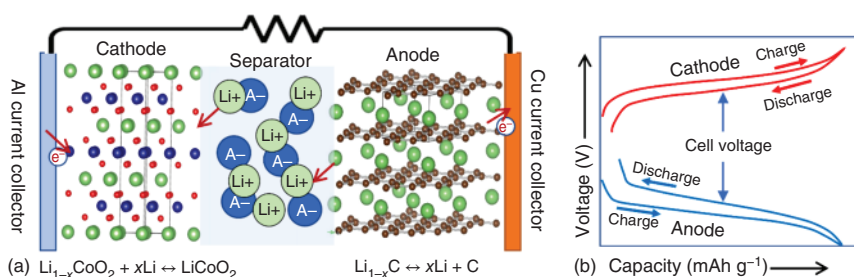


Figure 1.2 (a) Schematic of the working principle of a lithium-ion battery containing a LiCoO_2 cathode and graphite anode. (b) Qualitative voltage profiles during charge and discharge. Source: Belharouak et al. [3].

containing transition metal substitutions (e.g. $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$) have been developed to maximize the energy density and cycling stability of TMO cathodes. While most commercial Li-ion batteries contain graphite anodes, some systems also utilize TMO anodes such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The vast compositional landscape of TMOs explored as Li-ion active materials is detailed in Chapters 2, 3, 5, 7, and 16.

1.3 Brief History of Lithium-Ion Batteries

In the 1960s, intercalation chemistry was a prominent method used to alter materials' electronic and optical properties [4, 5]. For instance, the electronic conductivity of WO_3 can be varied several orders of magnitude by intercalating monovalent cations into the structure [6]. Rechargeable batteries which utilize ion intercalation reactions were first demonstrated in the 1970s by Whittingham [7] at Exxon Corporation. These prototype cells contained a layered TiS_2 cathode, lithium metal anode, and liquid electrolyte (e.g. LiClO_4 dissolved in a mixture of dimethoxyethane and tetrahydrofuran) [7]. One limitation of this system was the Li metal anode which forms dendrites that can penetrate the separator and internally short-circuit the cell. As an alternative anode, Yazami demonstrated reversible Li^+ intercalation in graphitic carbons using a polymer electrolyte in the 1980s [8]. However, in liquid electrolytes these intercalation anodes were hindered by solvent co-intercalation which resulted in graphite exfoliation and electrode degradation during cycling. In 1985, a group led by Yoshino at Asahi Kasei Corporation (Japan) identified petroleum coke anodes [9] which were stable during Li^+ insertion/removal, and these anodes were incorporated into Li-ion full cells containing liquid electrolyte. These discoveries ultimately led to the first commercial Li-ion batteries introduced by Sony in 1991. At around the same time, suitable electrolyte solvents (e.g. ethylene carbonate) which do not co-intercalate in graphite were also identified. Compared to disordered carbons derived from petroleum coke, graphitic anodes operate at more negative potentials which enables higher cell voltages and energy densities.

In addition to carbonaceous anodes, the 1980s also witnessed advancements in Li-ion intercalation cathodes. Notable examples include LiCoO_2 (Goodenough and coworkers) [10], LiMn_2O_4 (Thackeray and coworkers) [11], and polyanionic cathodes such as $\text{Li}_y\text{Fe}_2(\text{XO}_4)_3$, $\text{X} = \text{S}, \text{Mo}, \text{and W}$ (Manthiram and coworkers) [12]. These scientific breakthroughs enabled Li-ion batteries to dominate the rechargeable battery market for decades, and these systems are now ubiquitous in commercial devices ranging from portable electronics to electric vehicles. The 2019 Nobel Prize in Chemistry celebrated this achievement with an award to Profs. John Goodenough, Stanley Whittingham, and Akira Yoshino.

1.4 The Role of Advanced Characterization and Computing Resources

The rich history of Li-ion batteries demonstrates that translating scientific discoveries into viable energy storage systems requires decades of research and development.

Central to this development process are fundamental scientific discoveries (e.g. identifying structure/property correlations and understanding degradation mechanisms) needed to optimize material selection and system performance. Such efforts often require combining routine material characterization (e.g. electroanalytical methods, vibrational spectroscopy, and lab-source X-ray diffraction) with world-class instrumentation (e.g. X-ray/neutron beamlines). Several chapters in this book describe advanced characterization methods that enabled critical insights on TMOs for electrochemical energy storage, and examples include: (i) solid-state nuclear magnetic resonance spectroscopy (NMR) and electron paramagnetic resonance (EPR) to probe local bonding structure (Chapter 11), (ii) *in situ* and *operando* neutron diffraction to identify phase transformations during material synthesis and battery operation (Chapter 12), and (iii) X-ray spectroscopy and imaging to probe transition metal valence states (Chapter 13). In addition to these experimental efforts, advanced computing resources and machine learning (Chapters 14 and 15) have accelerated material discovery and provided mechanistic insight into processes occurring at length/time scales which are difficult to probe experimentally.

1.5 Beyond Lithium-Ion Batteries

The performance of Li-ion batteries is largely dictated by the active materials, and replacing the graphite anode with Li metal can enable batteries with specific energies $>400 \text{ Wh kg}^{-1}$ (compared to $\sim 200 \text{ Wh kg}^{-1}$ for today's commercial Li-ion batteries). As previously mentioned, formation of Li dendrites during charging presents major safety and reliability concerns, and to date, liquid electrolytes have been unable to effectively suppress Li dendrite formation. To combat this issue and stabilize the Li metal anode, there is growing interest in solid-state batteries (SSBs) containing solid electrolyte separators. Representative classes of solid-state Li^+ conductors include garnet oxides (e.g. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$), sulfides (e.g. $\beta\text{-Li}_3\text{PS}_4$ and $\text{Li}_6\text{PS}_5\text{Cl}$), polymers (e.g. poly(ethylene oxide) containing a Li^+ salt), and inorganic glasses (e.g. Lipon). The opportunities for Li metal are tremendous, but enabling practical SSBs requires overcoming major challenges related to material synthesis, processing, and interfacial stabilization as discussed in Chapter 8.

Energy storage costs are a primary factor in determining the viability of battery technologies for grid storage applications. While the cost of Li-ion batteries has decreased substantially in the past decade (e.g. from $\sim \text{US } \$1000/\text{kWh}$ in 2008 to $\sim \text{US } \$130/\text{kWh}$ in 2020), further cost reductions are needed to enable widespread adoption for large-scale stationary storage. Recent developments on low-cost rechargeable batteries discussed in this book include: (i) aqueous electrolytes for Li-ion systems (Chapter 6) and (ii) Na-based chemistries which utilize active material hosts that undergo intercalation, conversion, or alloying reactions (Chapters 3 and 4).

Development of next-generation energy storage systems is critical to combat climate change in the coming decades. Global energy consumption rates [13] are

expected to increase to 40.8 TW by 2050, and electrochemical energy storage systems represent one of the most promising platforms to bridge the supply/demand gap for intermittent renewable resources (e.g. solar and wind). In this regard, TMOs are expected to continue playing critical roles as components for low-cost, reliable energy storage to enable a sustainable future.

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References

- 1 Hayner, C.M., Zhao, X., and Kung, H.H. (2012). Materials for rechargeable lithium-ion batteries. *Annual Review of Chemical and Biomolecular Engineering* 3: 445–471.
- 2 Dunn, B., Kamath, H., and Tarascon, J.M. (2011). Electrical energy storage for the grid: a battery of choices. *Science* 334 (6058): 928–935.
- 3 Belharouak, I., Nanda, J., Self, E.C., et al. (2020). Operation, manufacturing, and supply chain of lithium-ion batteries for electric vehicles. <https://doi.org/10.2172/1737479>.
- 4 Gamble, F.R., Osiecki, J.H., Cais, M. et al. (1971). Intercalation complexes of Lewis bases and layered sulfides: a large class of new superconductors. *Science* 174: 493–497.
- 5 Aronson, S., Salzano, F.J., and Bellafore, D. (1968). Thermodynamic properties of the potassium-graphite lamellar compounds from solid-state emf measurements. *Journal of Chemical Physics* 49 (1): 434–439.
- 6 Whittingham, M.S., Michael, S., and Jacobson, A.J. (1982). *Intercalation Chemistry*. New York: Academic Press.
- 7 Whittingham, M.S. (1976). Electrical energy storage and intercalation chemistry. *Science* 192: 1126–1127.
- 8 Yazami, R. and Touzain, P. (1983). A reversible graphite-lithium negative electrode for electrochemical generators. *Journal of Power Sources* 9: 365–371.

- 9 Yoshino, A., Sanekata, K., Nakajima, T. (1987). Secondary battery. US Patent 4,668,595, filed 9 May 1986 and issued 26 May 1987, <https://patents.google.com/patent/US4668595A/en>.
- 10 Mizushima, K., Jones, P.C., Wiseman, P.J., and Goodenough, J.B. (1980). Li_xCoO_2 ($0 < x \leq 1$): a new cathode material for batteries of high energy density. *Materials Research Bulletin* 15: 783–789.
- 11 Thackeray, M.M., David, W.I.F., Bruce, P.G., and Goodenough, J.B. (1983). Lithium insertion into manganese spinels. *Materials Research Bulletin* 18: 461–472.
- 12 Manthiram, A. (2020). A reflection on lithium-ion battery cathode chemistry. *Nature Communications* 11 (1): 1550.
- 13 Lewis, N.S. and Nocera, D.G. (2006). Powering the planet: chemical challenges in solar energy utilization. *Proceedings of the National Academy of Sciences of the United States of America* 103 (43): 15729–15735.

