Understanding electrochemical potentials of cathode materials in rechargeable batteries

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Presently, sustainable energy as well as efficient and economical energy conversion and storage technologies has become important work in light of the rising environmental issues and dependence on portable and uninterrupted power sources. Increasingly more researchers are focusing on harvesting and converting solar energy, mechanical vibration, waste heat, and wind to electricity. Electrical energy storage technologies play a significant role in the demand for green and sustainable energy. Rechargeable batteries or secondary batteries, such as Li-ion batteries, Na-ion batteries, and Mg-ion batteries, reversibly convert between electrical and chemical energy via redox reactions, thus storing the energy as chemical potential in their electrodes. The energy density of a rechargeable battery is determined collectively by the specific capacity of electrodes and the working voltage of the cell, which is the differential potential between the cathode and the anode. Over the past decades, a significant number of studies have focused on enhancing this specific capacity; however, studies to understand and manipulate the electrochemical potential of the electrode materials are limited. In this review, the material characteristics that determine and influence the electrochemical potentials of electrodes are discussed. In particular, the cathode materials that convert electricity and chemical potential through electrochemical intercalation reactions are investigated. In addition, we summarize the selection criteria for elements or compounds and the effect of the local atomic environment on the discharge potential, including the effects of site energy, defects, crystallinity, and microstructure, using $LiMn_2O_4$, V_2O_5, Mo_6S_8, $LiFePO_4$, and $LiCoO_2$ as model samples for discussion.

Introduction

In addition to the rising concern of environmental pollution, modern society is becoming increasingly dependent on uninterrupted portable power sources for continuous Internet access and for working or collaborating with people across the globe. In spite of the efforts of both the research community and industries, the development of portable power devices has been painstakingly slow [1,2], falling behind the rapid advancements in electronic devices and electrically powered instruments and infrastructure. The industrial revolutions in the past centuries have led to unprecedented changes in social life, transportation, and production activities, with energy utilization reflecting the progress of industrial technology and human civilization. Fossil fuels, such as coal, crude oil, and natural gas, are used as primary energy sources to power all high-tech-dependent human activities. However, pollution arising from fossil fuel combustion has had a devastating impact on human health and the natural environment [3,4]. In addition, regardless of governmental policies or the fluctuation in price and supply, the natural reserves of fossil fuels are limited and not sustainable. Therefore, the focus of research has shifted to environmentally benign sustainable energy. Clean energy can be divided into three components: harvest and conversion of sustainable clean energy including solar energy, wind, mechanical vibration, and waste heat; energy storage typically in the form of

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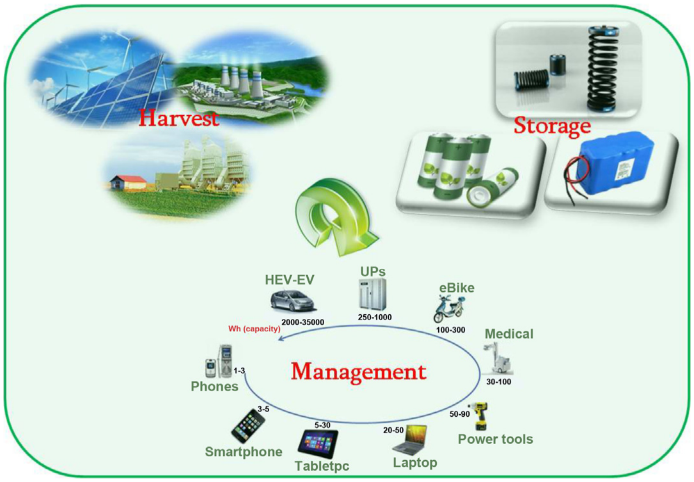

FIGURE 1

The energy utilization chain. Efficient harvest, storage, and management are three essential segments to energy consumption in modern society [5,33].

chemical potential including batteries, hydrogen, and biofuels; and management and efficient usage of energy including smart buildings and efficient lighting systems [5–10] (Fig. 1). Typical energy storage technologies, particularly for portable electronics and mobile instruments, are based on the conversion of electricity and chemical potential, as seen in fuel cells, batteries, and electrochemical pseudocapacitors, with the energy being stored in the form of chemical potential [6,11–13].

Due to their high energy density, batteries have long been used [14] to power portable electronics, as well as stationary and mobile instruments [15], such as lead acid batteries for automobiles [16]. In the last two decades, Li-ion batteries have advanced rapidly with increased energy density and long cyclic stability, which is beneficial for most portable electronics including mobile phones and laptop computers [16–19]. Current rechargeable batteries based on ion insertion/extraction in electrodes, including Li- [20–22], Na- [23–25], Mg- [18,26,27], and Al-ion [28,29] batteries, have been increasingly studied in both the academia and industry. However, sodium, magnesium, and aluminum have a lesser reducing effect than lithium (−2.71, −2.37, and −1.66 V vs. S.H.E., respectively, compared with −3.04 V for Li) as well as low gravimetric capacities (1165, 2046, and 2978 mAh/g, respectively; compared with lithium, 3850 mAh g^{-1}). Thus, devices based on metallic sodium, magnesium, or aluminum anodes have lower energy densities and operating voltages than those with lithium metal anodes [25,26,28]. To date, only Li-ion rechargeable batteries have been successfully commercialized and become an irreplaceable power source. In Li-ion rechargeable batteries, the cathodes that store lithium ions via electrochemical intercalation must contain suitable lattice sites or spaces to store and release working ions reversibly. Robust crystal structures with sufficient storing sites are required to produce a material with stable cyclability and high specific capacity [24,30]. In addition, a cathode with high electrochemical intercalation potential can be used to develop a high energy density battery with a given anode. This is because the energy density of the device equals the product of the specific capacity of the electrode materials and the working voltage that is determined by the differential electrochemical potentials between the cathode and anode [22,31]. This review focuses on secondary Li-ion batteries and their components to illustrate certain fundamental factors, in particular, the origin of the electrochemical potential of electrode materials and effective approaches to exploiting these electrochemical properties. In addition, the potential electrode materials for Na- and Mg-ion batteries are also discussed as the fundamental understanding acquired on Li-ion batteries will greatly benefit the increasing efforts on Na- and Mg-ion battery research [32].

Configuration and principle of Li-ion batteries

Li-ion rechargeable batteries consist of two electrodes, anode and cathode, immersed in an electrolyte and separated by a polymer membrane (Fig. 2). This basic device configuration has remained unchanged from the earliest developed batteries [34]. The similarities between Li-ion batteries and conventional batteries include the redox reactions at the interfaces between the electrolyte and electrodes, accompanied by the diffusion of ions in the electrolyte. However, the differences between conventional batteries, or galvanic cells, and Li-ion batteries are notable as well. In typical galvanic batteries, the redox reactions proceed simultaneously with the receding or advancing of the electrode surfaces, but not accompanied by either the solid-state mass diffusion in the electrodes or a change in the chemical composition and local atomic environment [35]. By contrast, the heterogeneous redox reactions in Li-ion batteries are always accompanied by solid-state

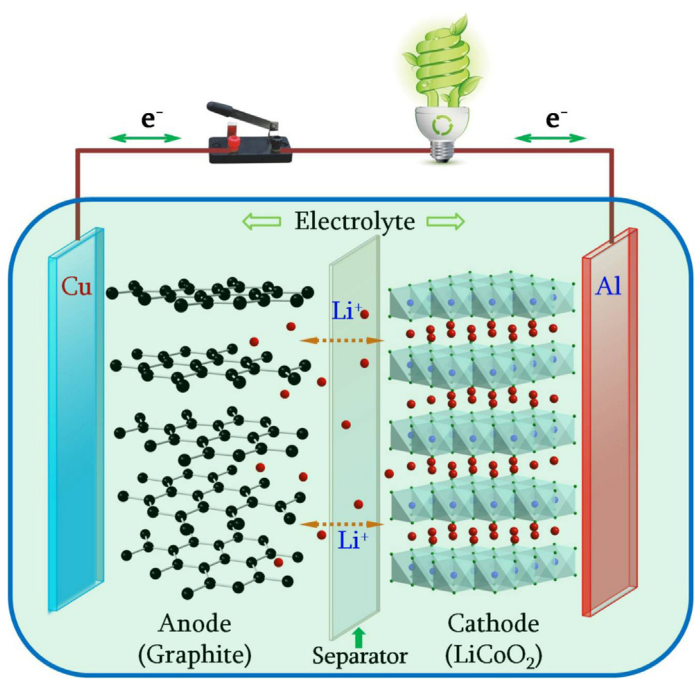

FIGURE 2

Schematic of the configuration of rechargeable Li-ion batteries. Na-ion, Mg-ion, or Al-ion batteries also have similar configurations, which differ from electrode materials [29,70,71]. For a Li-ion battery, as illustrated in the figure, Li ions are extracted from the cathode and inserted into the anode during the charge process, and the reverse reaction occurs during the discharge process. However, in a half-cell consisting of electrode material and lithium metal, Li ions are extracted from the electrode material and deposited on the surface of the lithium metal during the charge process, and Li ions are inserted into the host electrode material during discharge. Here, in practice, the electrode materials can be cathodes or anodes.