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Advance review on the exploitation of the prominent energy-storage element: Lithium. Part I: From mineral and brine resources

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ABSTRACT

Lithium (Li), an exceptional cathode material in rechargeable batteries, is an essential element in modern energy production and storage devices. The continuously increasing demand for lithium in these devices, along with their steady production, has led to the high economic importance of lithium, making it one of the strategically influential elements. The uneven distribution of mineral resources in the earth's crust and the unequal concentration in brine and sea water reserves also causes lithium exploitation to be of critical importance. This situation requires the efficient processing of lithium resources either by the processing of minerals/brine/sea water or by the recycling of spent lithium-ion batteries. To explore new routes for the sustainable exploitation of lithium, it is imperative to review the methodologies that have already been studied and are currently in industrial practice. In this study, we present an overview of the processes investigated for the extraction, separation and recovery of lithium from not only a technological perspective but also from a chemical perspective.

In Part I, this state-of-the-art review addresses the processing of lithium resources that currently contributes to the commercial exploitation of this energy-critical element. This review includes lithium recovery from mineral (spodumene, petalite, lepidolite, zinnwaldite) and brine resources. A deliberation of the mineralogical aspect along with a review of the extraction process of lithium minerals is subdivided according to the chosen media, namely, chloride, sulfate and carbonate, for their conversion into a leachable form, whereas the division of aqua-based resources is based on the lithium concentration. In the discussion, the advantages and/or disadvantages, problems and prospects of the processes are also summarized. We believe this article can contribute to improving the extraction and recovery processes of lithium toward the sustainability of this critical element and can provide future research directions.

Contents

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1. Introduction

Catastrophic climate changes, global warming and energy crises are substantial global challenges. The dependency on traditional fossil-based resources is one of the major causes of the energy crises. There is a consensus that countries cannot rely indefinitely on fossil-based energy sources; renewable energy must be developed as an alternative to meet the growing energy demands (UNDP, 2000; Rajasthan Renewable Energy, 2015). The conservation, storage and transmission of renewable energy require the availability of suitable devices. Batteries have been considered suitable candidates for power sources in large and portable applications. For any battery, the most critical feature is the capability of storing a large amount of energy within a given volume-to-mass ratio in a short period (J.S. Kim et al., 2014; H. Kim et al., 2014). For this purpose, lithium (Li, with a very low density of 0.534 g/cm^3 combined with a high electrochemical standard potential of −3.04 V) (Hart and Beumel, 1973) has found applications in rechargeable batteries as an exceptional cathode material. Currently, lithium ion batteries (LIBs) are the most promising rechargeable batteries due to their unmatched characteristics to capture energy compared to the other technologies (Table 1) (Salil, 2012; Wagner, 2006). Moreover, as a blanket material in the fuel regeneration of fusion energy reactors, the large amounts of energy carried by the neutrons would be transferred to the excess lithium and then recovered by a heat exchanger (Lithium World Nuclear Association, 2014).

In addition to the major applications in glass and ceramics (35%), rechargeable batteries (29%), lubricating grease (9%), air treatment by CO_2 capture (5%), continuous casting mold flux powders (6%) and polymer production (5%) (Jaskula, 2013), the unprecedented growth in direct plug-in hybrid vehicles is projected to increase the demand for lithium in LIBs by >30% by 2020 (Ping et al., 2014; Forster and Rutherford, 2011). The role of lithium in the fulfillment of the global energy demand is vital for the energy age of tomorrow. Fig. 1 presents the future demand and supply of Li_2CO_3, which is often used in battery materials. A shortage is projected to occur around 2020 (Critical Materials Strategy, 2010). The mitigation of the supply risk in clean energy requires more than 1.5-fold of Li_2CO_3 in 2025 than in 2015 (∼265 kilo tons) (Critical Materials Strategy, 2010; Fox-Davies Resources Specialist, 2013). This enormous demand projection indicates the greater economic importance of lithium than of silver (ECEI-Report, 2010), even though lithium is the 25th most abundant element (20 mg/kg) in the earth's crust, with total reserves of 13,000 kilo tons (including brine) worldwide (Jaskula, 2013; Fox-Davies Resources Specialist, 2013). The high economic importance and the capability to transform the methods of production, transmission, storage, or energy conservation have placed lithium among the strategically influential elements, called the "energy-critical elements", because of the significant uncertainty related to time delays in the production and utilization of lithium (Fox-Davies Resources Specialist, 2013; ECEI-Report, 2010; ECEs-Energy Critical Elements, 2011).

The global production and consumption data of lithium from its resources are shown in Fig. 2 (Polinares EU Policy on Natural Resource, 2012; USGS, 2014; USGS Mineral Yearbook, 2013; Mohr et al., 2012). The efficient processing of resources is complicated largely because of the low concentration of lithium in sea water (as low as 0.1–0.2 ppm) (Brown, 2010; Shahmansouri et al., 2015) and the need for beneficiation to upgrade the rock-minerals followed by an energy-consuming heat treatment (usually at or above 800 °C) prior to lithium dissolution into aqueous media (Luong et al., 2013). The aqueous solutions always contain high levels of impurities, which make downstream processing difficult. In general, the traditional separation technologies are considered amateurish, unfriendly to the environment and unsustainable. Therefore, improving the separation and processing of lithium from primary and secondary resources is necessary. Hence, to explore new methods of lithium exploitation, both technologically and economically, it is imperative to review the methodologies that have already been explored. It has been nearly

Table 1
Application of lithium ion batteries (Salil, 2012; Wagner, 2006).

Battery type	Specific energy density (W h/kg)	Specific power (W/kg)	Life span cycles	Major application areas
Li-ion	100–265	250–340	400–1200	Laptop, computers, mobile devices, modern electric vehicles
Ni–Cd	40–60	150	∼2000	Cordless & wireless telephones, emergency light
Ni–Zn	100	>3000	400–1000	Cordless telephones, digital cameras, battery operated lawn
Pb-acid	33–42	180	500–800	Automotive engine ignition