НАУЧНАЯ СЕКЦИЯ «ПРИБОРОСТРОЕНИЕ. МАШИНОСТРОЕНИЕ. МЕТАЛЛУРГИЯ. СТРОИТЕЛЬСТВО»

УДК 69.04

EXTRACTION OF VALUABLE LANTHANUM, ZIRCONIUM AND LITHIUM ELEMENTS FROM SOLID ELECTROLYTE $LI_7LA_3ZR_2O_{12}$ (LLZO)

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Summary. *Valuable elements in lithium-ion batteries is a very significant secondary resource. Based on the recovery and recycling of the spent all-solid-state lithium-ion batteries in the future, we explore extracting valuable lanthanum, zirconium, and lithium elements from the solid electrolyte tetragonal phase LLZO by the leaching with the dilute sulfuric, and then by precipitation methods of double salts and carbonate salt, and recrystallization, respectively.*

The all-solid-state lithium-ion battery (SSB) was developed, owing to high energy density, good safety, and little influence by external temperature, and is one of the most competitive energy storage batteries in the future [1, 2]. Therefore, the huge number of spent SSB will also danger our life environment like that of spent LIBs nowadays if SSB can completely replace LIBs in the future.

As well known, the solid-state electrolyte is the key material of SSB battery, which mainly includes lithium phosphorus oxynitride (LiPON) type, lithium fast ion conductor (LISICON) type, sodium fast ion conductor (NASICON) type, etc. Among them, the solid cubic garnet $Li_7La_3Zr_2O_{12}$(LLZO) inorganic electrolyte is popular and has potential for application because of its simple synthesis process, stable chemical and electrochemical properties, high ionic conductivity at room temperature, and good compatibility with electrodes [3–6].

Based on both no spent commercial LLZO-type lithium battery nowadays and the simplicity of phase transformation from cubic to tetragonal-phase, herein, we directly investigate the extraction of the valuable La, Zr, and Li elements in the solid electrolyte quadratic-phase LLZO by conventional hydrometallurgy methods.

Lithium hydroxide ($LiOH \cdot H_2O$), lanthanum oxide (La_2O_3), zirconia (ZrO_2), and isopropanol (C_3H_8O) were used to prepare the tetragonal LLZO solid electrolyte. Concentrated sulfuric acid (H_2SO_4 98wt%) was diluted to 0.5 mol/L for leaching the self-made solid electrolyte tetragonal phase LLZO.

Acid leaching and recovery of lanthanum, zirconium, and lithium elements in the tetragonal phase LLZO.

Preparation and characterization of the tetragonal phase LLZO.

Tetragonal phase LLZO was prepared by the solid-state sintering method [7].

Acid leaching of the tetragonal phase LLZO.

The 2.09 g self-made LLZO was immersed into the 0.5 mol/L dilute sulfuric acid with a stirring rate of 400 r/min. The contents of valuable La, Zr and Li elements in the filtrate analyzed by atomic absorption spectrophotometer (TAS-990 AAS) were used to calculate the leaching rate of the LLZO, the equation as follows:

$$\mu(\%) = \frac{c \times V}{m} \times 100\ \% \qquad (1)$$

μ – Leaching rate of the LLZO; c – Lithium element concentration in leaching solution; V – Volume of acid leaching solution; m – Mass of lithium element in the LLZO.

The double salt precipitation method was employed to extract lanthanum elements from the leaching solution. As a precipitant, sodium hydroxide was added to the above acid leaching solution to form $La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$ double salt precipitation. The equation of extraction rate of lanthanum element is as follows:

$$\varphi(\%) = \frac{\alpha}{\beta} \times 100\ \% \qquad (2)$$

φ – Extraction rate of lanthanum element; β – Mass of lanthanum element in the leaching solution; α – Mass of lanthanum element in the dried sodium lanthanum sulfate double salt.

The precipitation method was employed to recover the zirconium element from the above filtrate. The equations of extraction rate of zirconium, and lithium elements are as follows, respectively:

$$\gamma(\%) = \frac{a}{b} \times 100\ \% \qquad (3)$$

γ – Extraction rate of zirconium element, *a* – Mass of zirconium element in zirconium carbonate, *b* – Mass of zirconium element in the filtrate recovered lanthanum.

$$\delta(\%) = \frac{c}{d} \times 100\ \% \qquad (4)$$

δ – Extraction rate of lithium element, *c* – Mass of lithium element in lithium carbonate, *d* – Mass of lithium element in the purified filtrate.

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УДК 69.04

21世纪海上丝绸之路”建设面临的挑战与对策

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Summary. *In the 21st century, the change of the international marine strategic situation provides both opportunities and challenges for China's strategy of building a powerful marine country. Against this background, China has implemented the strategy of the “21st Century Maritime Silk Road”. Focuses on the analysis of the achievements and challenges of China's “21st Century Maritime Silk Road” construction, and puts forward corresponding countermeasures based on the analysis.*