Extraction of Potassium from Biotite by Lithium Ion Exchange and Its Electrochemical Properties

Yilin Cheng, Zhiliang Huang*, Donghui Yao, Changsheng Wu
School of Materials and Engineering, Wuhan Institute of Technology, Wuhan 430205, China
* hzl6455@126.com

Abstract: In order to solve the problem of shortage of potassium resources in China, the technology of extracting soluble potassium from insoluble potassium minerals needs to be further studied. Biotite with relatively high potassium content was used as the research object to extract soluble potassium elements from biotite by lithium ion exchange method, and the electrochemical properties of biotite were tested after potassium extraction. After 80°C hydrothermal reaction for hours, potassium and lithium ion exchanged with each other, and soluble potassium were obtained from the filtrate by filtering the reaction liquid. The efficiency of potassium extraction and the structure of mica changed after the oxidation reaction was determined by XRF and XRD, respectively. The results showed that the layered silicate structure of mica after the reaction was not destroyed, and the potassium extraction rate for 8h was up to 92.3%. The discharge capacitance was 1.32F /g, and the coulomb efficiency was 64% in 0.6C.

1. Introduction
China is not only a large agricultural country, but also a large potassium shortage country. Potassium is mainly used to make potash fertilizer, which is one of the three major fertilizers used in China's agricultural production. It is not only the promoter of crop growth and development, but also can help crops resist diseases and insects [1-3]. After 60 years of development and construction, China's potash self-sufficiency rate has been close to 60%, China's potash reserves are only 2.2% of the world's reserves, but the agricultural land area is 8% of the world's total arable land. In recent years, the annual consumption of potassium resources in China continue to increase, all of which indicates that the shortage of potassium resources is facing severe challenges [4-7]. Potassium resources are mainly divided into two types: insoluble potassium minerals and soluble potassium minerals. The soluble potassium resources are mainly divided into two types: soluble solid potassium mineral, soluble liquid salt lake brine or sea water [8], The present potassium in China mainly comes from soluble potassium resources [8]. Mainly refers to the difficult soluble potassium resources exists on the form of the silicate mineral potassium, have made it clear in our country at present difficult soluble potassium resources reserves of more than 10 billion tons [9-11], but such difficult soluble potassium resources are not being efficient exploitation and utilization, it is a waste of resource, therefore, effective use of difficult soluble potassium resources to mention potassium can alleviate the potassium to the problem of shortage of resource supply and demand.

At present, the commonly used potassium extraction methods are all carried out under the premise of destroying the layered structure of mica [12], but this method is not conducive to the rational
utilization of resources. So we need to extract potassium in a way that doesn't destroy the mica layer [13]. Mica octahedral space often have variable valence of ions, such as ferrous iron ion, etc., under the condition of hydrothermal alumina eight sides position variable valence ion of oxidation reaction, making it the price increases, decreases the electronegativity of mica tetrahedron lamella, reduce potassium by coulomb force, make it easier for potassium ion is replaced [14-15]. Lithium ions that replace inter-layer potassium ions exist in the form of large-radius hydrated lithium ions in the inter-layer of mica. The enclosed water molecules slightly support the mica lamellar layer, increase the spacing between the layers, and broaden the exchange channels of potassium lithium ions. This "space effect" can further promote the exchange process of potassium lithium ions. This method changes the valence bond between potassium and cation between mica layers and produces the coulomb effect. These two effects can be used to replace potassium ion by replacement ion lithium ion, and will not destroy the layered structure of mica, which is conducive to the comprehensive utilization of resources.

This experiment chooses high potassium content of biotite (biotite K₂O mass fraction is 8% - 11%) in the preparation of hydrated lithium mica as the research object, the biotite under hydrothermal conditions, oxidation treatment on it after oxidation treatment of biotite tetrahedron layer between potassium ions replaced by lithium ion, lithium ion in the interlayer exist in large radius hydrated lithium ion, package of water molecules slightly opens black mica sheet layer, but won't destroy the layered structure of mica. The electrochemical properties of lithium mica hydrate after potassium extraction were studied by constant current charge-discharge and cyclic voltammetry.

2. Experiment

2.1. Experimental materials
Biотite: bought from Lingshou mining company of China, it is dark green in flake, with better gloss and purity of 99%. It needs to be ground into powder for use.

Lithium nitrate: purchased from sinopsin group of white powder form.

Dilute hydrochloric acid: concentrated hydrochloric acid in laboratory is diluted with distilled water at a concentration of 0.5mol/L.

2.2. Experimental instruments
Electronic balance, constant temperature water bath pot, constant temperature magnetic stirrer, circulating water vacuum pump, constant temperature vacuum drying box

2.3. Experimental process
Ion exchange experiment: eight time points of 1h, 2h, 3h, 4h, 5h, 6h, 7h and 8h were taken as a group of time gradients. Other conditions were consistent. Scales on the analysis of the said take 1.0 g biotite mineral powder , biotite will mica mineral powder in 250 ml conical flask, and then slowly pour 200 ml nitric acid lithium saturated solution, and then by drop to 0.5 mol/L dilute hydrochloric acid, adjust PH value of 4, mixing, after sealing the conical flask in 80 °C constant temperature water-bath water mixing, every 1 h conical flask, collect after get the sample of the reaction, called a hydrated lithium mica.

2.4. Characterization methods
2.4.1 X-ray diffraction analysis. Using X-ray diffraction (X - ray diffraction, hereinafter referred to as XRD, instrument types: Bruker D8 ADVANCE, origin Germany) structure characterization of the samples, the working voltage of 40 kv, X-ray wavelength of 0.15418 nm, working current is 40 ma, scanning speed is 6 ° / min, 5° to 50° scan Angle.

2.4.2 electrochemical performance test. Take 40mg of finished biotite, add 50mul 3% polytetrafluoroethylene binder and 5mg acetylene black, place the mixture in agate mortar and grind it fully, press the mixture into thin slices under certain pressure, and then cut the thin slices into a square film, the film thickness is about 0.5mm, long is 1cm, wide is 0.5cm.
Platinum sheet electricity is used as the auxiliary electrode, silver chloride as the reference electrode and square membrane as the working electrode. 1mol/L KOH solution is used as the electrolyte to form the capacitor.

The electrochemical performance of the square diaphragm was tested by an electrochemical workstation of CS2350 produced by Wuhan Coster instrument co., LTD. Electrode specific capacitance is calculated by the following formula:

\[ C = \frac{2I\Delta t}{m\Delta V} \]  

Where, \( C \) is the specific capacitance of a single electrode, F/g; \( I \) is charge and discharge current, A; \( t \) is charging and discharging time, s; \( m \) is the mass of hydrated lithium mica in the electrode, g; \( V \) is the voltage change within charging and discharging time, V.

3. Results and discussions

3.1. Effect of reaction time on potassium extraction rate

XRD characterization of biotite mineral (B0) and hydrated lithium mica (B2, B4, B6, B8) was carried out to analyze the phase changes of mica. The results are shown in figure 1(a).

Can be seen from figure 1(a), biotite ore of hydration lithium mica samples (001) \( (d = 1.006 \text{ nm}) \) characteristic peak almost disappeared, a new (001) * \( (d = 1.275 \text{ nm}) \) characteristic peak, biotite layer spacing expanded about 0.27 nm, this is because the "coulomb effect" and "space effect", under the action of replace potassium ions between the layers of lithium ion in biotite between layers in the form of large radius of hydrated lithium ion, lithium ion slightly opens biotite hydrate interlayer, makes the interlayer spacing. The characteristic peaks of the hydrated lithium mica and biotite after ion exchange are sharp and obvious, which indicates that the layered structure of biotite is not destroyed by the lithium exchange reaction, which is beneficial to the comprehensive utilization of mica.
As can be seen from the figure 1 (b), reaction time and the relation curve of the rate of potassium can be divided into two parts, the first part is the early stage of the reaction of potassium rate change is bigger, this is because in the process of ion exchange, hydrated lithium ions into the layer, the layer spacing between widened potassium lithium ion exchange channel, weakened the potassium ions between the layers by coulomb force, improve the potassium ion exchange rate. The second part is the late reaction period, and the potassium extraction rate changes little. Due to the limited interlayer space and concentration difference, the potassium extraction rate slows down, and reaches the highest rate after 8h, which is 92.3%.

3.2. Electrochemical properties of hydrated lithium mica
Figure 2 (a) shows the charge and discharge curve of lithium mica hydrate under the 0.2C multiplier. It can be seen that a total of 18s is required for the first charge and discharge, and the charge and discharge time is significantly shorter than the discharge time. According to the curve data, according to equation (1), the specific capacity of the first discharge of lithium mica hydrate (charge and
The discharge current is 0.8mA at the rate of 0.2C is calculated as 6.4F/g, the coulomb efficiency of the first charge and discharge is 6.25%, the specific capacity of the discharge in the eighth charge and discharge cycle is 4F/g, and the coulomb efficiency is 20%. With the increasing of charge and discharge times, the coulomb efficiency is higher and higher. The specific discharge capacity of biotite raw ore was 0.32F/g at the rate of 0.2C. After modification, the specific discharge capacity of biotite ore was significantly increased, showing good electrochemical performance.

Figure 2 (b) compares the first cycle charge and discharge curves at 0.4C and 0.6C multiplicative rates. It can be seen that the charging and discharging time decreases with the increase of multiplier. It takes 18s for the first charge and discharge of the hydrated lithium mica anode material at a rate of 0.2C. It takes 3.3s and 1.8s for the first charge and discharge at a rate of 0.4C and 0.6C, respectively. According to equation (1), the discharge specific capacity at the rate of 0.4C and 0.6C is 2F/g and 1.32F/g respectively, and the coulomb efficiency for the first charge and discharge is 40% and 64% respectively. It can be seen that with the increase of the rate, the specific capacity for the first discharge becomes smaller and the coulomb efficiency becomes higher and higher.

![Figure 3](image)

**Figure 3.** Cyclic voltammetry graphs of hydrated Li-mica at the scanning rate of 100mV/s.

Figure 3 shows the cyclic volt-ampere curve of the first three cycles of hydrated lithium mica anode material at the scanning rate of 100mV/s. As shown in Figure 3, during the first three cycles, the positions and intensity of oxidation peak and reduction peak are basically unchanged, with a strong reduction peak at -0.85v and a weak oxidation peak at -0.65v. The redox peak corresponds to the lithium removal process of hydrated lithium mica. If the cyclic voltammetry curve in Figure 3 is asymmetric, the electrode reaction is irreversible.

Figure 4 shows the cyclic voltammetry curves of hydrated lithium mica anode material at scanning rates of 50, 100 and 150mV/s. As shown in Figure 4, the positions of oxidation and reduction peaks do not change at different scanning speeds, but the intensity changes, and the peak current also increases with the increase of scanning rate. According to the electrochemical theory, for the diffusion controlled electrode process, the peak current is proportional to the scanning speed to the power of one half. With the increase of scanning speed, the specific capacity of hydrated mica decreases. This is because at the higher scanning speed, there is less chance for the electrolyte ions to interact with the inner surface of the electroactive material.
4. Conclusion

Potassium is extracted from biotite by ion exchange method, which takes a short time and has a good potassium extraction effect without damaging the layered structure of biotite. The maximum K⁺ of 92.3% can be extracted within 8h, and the hydrated lithium mica anode material is also prepared. The specific surface area of lithium mica hydrate as a negative electrode material is only 125cm²/g, but when constant current charge and discharge is carried out at the rate of 0.6c, the discharge specific capacity of lithium mica hydrate negative electrode material can reach 1.32F/g, and the coulomb efficiency is 64%, indicating that modified lithium mica hydrate has a good development prospect in the field of electrode materials.

Acknowledgments

This project was supported by the National Natural Science Foundation of China (51374155) and the Hubei Province Key Technology R&D Program (2014BCB034) and Tenth Graduate Education Innovation Fund of Wuhan Institute of Technology (CX2018055). This work acknowledges the support of the Analysis and Test Center of Wuhan Institute of Technology.

References

[1] Perrenoud S 1990 Potassium and plant health Basel, Switzerland: International Potash Institute
[2] Sardar A, Ashraf M, Akhtar M E 2009 Effect of Potash on N, P and K Content of Young Mature Leaves and Nitrogen Utilization Efficiency in Selected Cotton Varieties Pakistan Journal of Biological Sciences 6 9
[3] Sharma S, Duveiller E, Basnet R, et al. 2007 Effect of potash fertilization on Helminthosporium leaf blight severity in wheat, and associated increases in grain yield and kernel weight Field Crops Research 93 142
[4] Davide C, David A C 2015 Manning, Antoine Allanore. Historical and technical developments of potassium resources Science of the Total Environment 2015 502
[5] Davide C, Marcelo de O, Rebecca M 2017 Stokes, Taisiya Skorina, Antoine Allanore. Characterization of potassium agrominerals: Correlations between petrographic features, comminution and leaching of ultrapotassic syenites Minerals Engineering 2017 102
[6] Ciceri D, Manning D A C, Allanore A 2015 Historical and technical developments of potassium resources Science of The Total Environment 502 590
[7] Gill M A, Ahmad M I, Yaseen M 1997 Potassium-deficiency stress tolerance and potassium utilization efficiency in wheat genotypes Springer Netherlands, 1997

[8] Warren J K 2016 Potash Resources: Occurrences and Controls Evaporites. Springer International Publishing

[9] Li L, Lei S, Liu Y, et al. 2016 Extraction and reaction mechanism of potassium from associated phosphorus and potassium ore Journal of Wuhan University of Technology-Mater. Sci. Ed. 31 1255

[10] Jalali M, Zarabi M 2006 Kinetics of nonexchangeable-potassium release and plant response in some calcareous soils Journal of Plant Nutrition and Soil Science 169 196

[11] Tomita K 1972 Formation of an Interstratified Mineral by Extraction of Potassium from Mica with Sodium Tetraphenylboron Clays and Clay Minerals 20 225

[12] Meng P, Li Z, Huang Z, et al. 2017 Extraction of potassium from biotite by Ba$^{2+}$/K$^+$ ion exchange and the structural transformation Physics & Chemistry of Minerals, 43 (6) 1

[13] Sun Y, Feng F, Liang W 1990 Chemistry of marine resources: XVI. A new potassium reagent and its enrichment behaviour for potassium ion in seawater Acta Oceanologica Sinica 9 (2) 263

[14] Wan G Z, Wang Y, Chen J F 2016 Potassium extraction from potassium bearing shale in phosphate ore by wet coupled sulfuric acid and phosphoric acid Industrial Minerals & Processing 1 12

[15] Song S K, Huang P M 1988 Dynamics of Potassium Release from Potassium-Bearing Minerals as Influenced by Oxalic and Citric Acids Soil Science Society of America Journal 52 383