Extraction of Potassium from Biotite by Sr$^{2+}$/K$^+$ Exchange Method and Electrochemical Properties of Hydrated Sr-Mica

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Abstract: Soluble potassium has been successfully extracted from biotite by Sr$^{2+}$/K$^+$ ion exchange. The hydrated Sr-mica after ion exchange has better electrochemical properties. The potassium extraction rate, mica silicate structure and electrochemical properties (charge-discharge and cycling properties) before and after ion exchange were characterized by X-ray fluorescence spectroscopy, powder X-ray diffraction, Fourier Transform Infrared spectrometer and constant current charge-discharge cycle technology. The results show that after 10 hours of strontium ion exchange, the layered silicate structure is not destroyed. The maximum potassium extraction rate is 98%. The biotite gradually transforms into vermiculite strontium mica to form strontium mica, and the basal (001) spacing expands from 1.001 nm to 1.517 nm. The electrochemical properties of hydrated Sr-mica obtained after exchange have been improved.

1. Introduction
As a strategic mineral resource, potassium salt plays a vital role in agriculture, medicine and industry. Potassium salt is one of the important foundations of national economic development. Potassium is very important in agricultural production. But most of the land is deficient in potassium in China. About one third of the cultivated land is deficient in potassium or seriously deficient in potassium in China, especially in southern China. In the medium and long term, demand of potassium fertilizer will continue to rise at an average annual rate of 5-6% in China. However, Self-sufficiency rate of potassium fertilizer is only 58% in China. The country’s annual import of potassium fertilizer is about 6 million tons. It will continue to grow every year. We can see that China is experiencing the crisis of potassium deficiency [1-3].

Layered aluminosilicate mineral is an economic clay. There are Kaolinite, smectite and mica. Kaolinite and smectite have been widely studied due to their expandable interlayers which confesses them applications as host of noble metal catalyst [4-6]. The research on the clays in mica group, however, shall not be neglected though they were relatively less attractive due to the stable crystalline structure which derives from the strong covalent bonding between potassium and the aluminosilicate sheets [7,8]. The chemical stability of the micaceous clay, on the other hand, admits micaceous clays good electrochemical properties which indicates its applications in functional materials such as insulators and UV shield material.
2. Experiment

2.1. Materials
Biotite which shows dark green color was purchased from Lingshou, Hebei Province, China. It ground into 200 mesh powder. Sr(NO₃)₂ was purchased from Sinpharm Chemical Reagent Co.,Ltd. Hydrochloric acid solution (0.5 mol/L) which is for the pH adjustment was prepared in laboratory. And distilled water was prepared in laboratory.

2.2. Experiments
One gram biotite powder (B₀) and 200.0 mL saturated Sr(NO₃)₂ solution was mixed in a 250.0 mL conical flask. Then, the pH of the solution was adjusted to 1.0 with 0.5 mol/L hydrochloride. Afterwards, the conical flask was tightly sealed and put in a water bath at 80°C by magnetically stirring for different times. When reaction completed, a filtration was performed immediately with a resin filtering membrane and the residue was washed with distilled water until no residual Cl⁻ and Sr²⁺ was detected. Subsequently, the sample was dried in an oven at 80 °C for 12 h. The obtained samples were marked B₀-B₁₀ according to the reaction time, for example, B₃ means the sample was obtained from a reaction of 3 hours.

2.3. Characterization
X-ray fluorescence spectrometry (Panaco Axios, Dutch) was used to determine the chemical composition of biotite and Sr(NO₃)₂-treated biotite. Test parameters was rhodium target. Scanning time was 20 minutes.

The Powder X-ray Diffraction (D8 ADVANCE, Brucker, Germany) was used to characterize the structural changes of the samples. The acceleration voltage was 40kV and the acceleration current was 40 mA. The X-ray wave length was 1.540 Å. The scanning angle is from 2 to 50 degree, the scanning velocity was 0.01023 degree per step.

A Fourier Transform Infrared spectrometer (Nicolet Impact 6700) with a resolution of 4K was used to characterize the change of group valence bond structure. The scanning range is 4000-400 cm⁻¹. The sample was amounted on a KBr disc, and the sample used was measured as 2% wt. of the KBr.

3. Results and discussions
As shown in table 1, most of potassium in biotite (B₀) were replaced after being treated with Sr(NO₃)₂ for 10 h. The ratio of Si/Al/Fe almost remained unchanged before and after, meaning the basic crystalline structure of biotite is intact. The chemical formulas of B₀ and B₁₀ were calculated by using the structural formula method [9], as shown in table 2. According to the results, 98% of the K⁺ in biotite is replaced by Sr²⁺.

| Table 1. The chemical composition (wt%) of B₀ and B₁₀. |
|-------------|---------|---------|---------|---------|---------|---------|---------|
|            | SiO₂    | Al₂O₃   | Fe₂O₃   | MgO     | K₂O     | SrO     | F       | Loss    |
| B₀(biotite) | 35.9    | 13.3    | 16.7    | 19.0    | 11.4    | 0       | 2.8     | 0.9     |
| B₁₀(Sr-biotite) | 45.9 | 11.2    | 12.5    | 16.68   | 0.3     | 3.79    | 2.7     | 6.93    |

| Table 2. Chemical formula of B₀ and B₁₀. |
|-------------|-------------|
| Sample      | Formula     |
| B₀(biotite) | (K₁.36Na₀.08)(Mg₂.67Fe₁.18Al₀.48)(Al₁.00Si₃.00O₁₀)[F₀.83(OH)₁.17] |
| B₁₀(Sr-biotite) | (K₀.00Na₀.00Sr₀.69)(H₂O)₁₀(Mg₁.52Fe₀.7)(Al₁.00Si₃.00O₁₀)[F₀.63(OH)₁.37] |

After 0-10 h Sr²⁺/K⁺ exchange, the layered structure of biotite remained unchanged. But the spacing of characteristic crystal (001) plane d(001) changed. As shown in Figure 1, after 1-6 h Sr²⁺/K⁺ exchange, the characteristic diffraction peak indexed as (00l) plane of biotite were significantly
weakened. At the meantime, some new diffraction peaks appeared: the first one was marked as (001)*. The spacing of (001) plane is enlarged from 1.006 nm ($d_{(001)}$) to 1.517 nm ($d_{(001)*}$). This is due to the ion exchange of K$^+$ by hydrated Sr$^{2+}$, which enlarged the spacing between layers and began to form vermiculite layers. However, Sr$^{2+}$/K$^+$ is not completely exchanged at this time. So the diffraction peaks (001), (003), (004), (005), (001)*, (004)* and (005)* coexisted.

In the reaction of 6-10 h, the relative intensities of characteristic diffraction peak indexed as (00$l$)/ plane of product continued to weaken. The characteristic diffraction peak indexed as (00$l$) plane of product increased gradually. The characteristic diffraction peak indexed as (00$l$) plane of product continued to weaken. After 10 h Sr$^{2+}$/K$^+$ exchange, the characteristic diffraction peak indexed as (00$l$) plane of Ba almost disappeared. There were five new diffraction peaks ( (001)**, (002)**, (003)**, (004)** and (005)** ) left. It shows that Sr$^{2+}$/K$^+$ was completely exchanged and vermiculite-type hydrated Sr-mica was formed.

**Figure 1.** XRD patterns of products obtained at different reaction time.

**Figure 2.** Middle-FTIR patterns samples of B0, B10.
To understand the structure of vermiculite-type hydrated Sr-mica, the FTIR tests were used. As can be seen in Figure 2, the stretching vibration peak ($\nu_{\text{H}_2\text{O}}$) and bending vibration peak ($\delta_{\text{H}_2\text{O}}$) of water molecule in $\text{B}_{10}$ are obviously stronger than those in $\text{B}_0$ [10,11]. It further confirmed the existence of structural water and vermiculite layer in $\text{B}_{10}$.

The electrodes were assembled with biotite and hydrated Sr-mica and were charged and discharged at constant current. Charging and discharging curves of biotite and hydrated Sr-mica at 0.05 C multiplier are shown in Figure 3. Charging and discharging properties of biotite electrodes can be seen in Figure 7(a). The curves show triangular symmetry distribution, indicating that the charging and discharging reversibility of biotite electrodes is good. Under constant current charging and discharging conditions, the voltage varies linearly with time. It shows that the reaction of biotite electrode is mainly the charge transfer reaction on the double layer. The discharge time is only 2.5 s. According to the curve data, the specific capacitance of biotite electrode can be calculated as 0.33 F/g. Figure 7(b) shows that the discharge time of hydrated Sr-mica electrode is 5.6 s. The specific discharge capacity is 2.35 F/g. This indicates that the modified mica structure has a good future in the field of electrode materials. It can be applied to small capacitance electrode materials such as button batteries.

![Figure 3](image_url)

**Figure 3.** (a) Cycling charge-discharge curve of biotite at 0.05 C. (b) Cycling charge-discharge curve of Sr-biotite at 0.05 C.

### 4. Conclusion

1. After 10 h Sr$^{2+}$/K$^+$ exchange, the biotite transformed into vermiculite-type hydrated Sr-mica. About 98% of K$^+$ in biotite was replaced by Sr$^{2+}$. And almost half of the interlayer cations are occupied by Sr$^{2+}$, leaving another half vacancies. The “vacancy effect” promotes the exchange rate of Sr$^{2+}$/K$^+$ in the early stage of the reaction.

2. Because of the formation of hydrated Sr$^{2+}$ between layers, the base (001)* spacing of vermiculite-type hydrated Sr-mica increases to 1.517 nm compared with the base (001) spacing of biotite at 1.066 nm.

3. Hydrated Sr-mica obtained after Sr$^{2+}$/K$^+$ exchange has a charge-discharge performance. At constant current of 0.05 C, the specific capacitance is 2.35 F/g. This opens up a new way for the future application of biotite.

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