IFS. Pub-23

Proceedings to 29th Technical Sessions of Geological Society of Sri Lanka, 2013, 101-104

Purity Enhancement of Sri Lankan Vein Graphite for Lithium - ion Rechargeable Battery Anode

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1. Introduction

Graphite has recently attracted considerable attention as an attractive candidate for anode material in lithium-ion rechargeable batteries (LIB). However, presence of impurities in graphite inevitably results in reactions with the electrolyte that leads to decomposition and anode ageing in LIB (Zaghib *et al.*, 2003; Vetter *et al.*, 2005). Therefore, most of the practical LIBs use expensive synthetic graphite as the anode material even though natural graphite is cheap and abundant. Consequently, many researchers have focused on removing impurities in natural graphite to create a highly ordered crystalline structure with exceptional purity (Fu *et al.*, 2006; Shui *et al.*, 2006).

Vein type graphite deposits in Sri Lanka are considered as a unique occurrence of graphite because of its high purity, extensive mineralization and restricted occurrence. Vein graphite in these deposits has been categorised into four structurally distinct graphite varieties (Balasooriya *et al.*, 2006,2007). Graphite with 95-99% of carbon and gangue minerals such as pyrite, chalcopyrite, calcite, biotite and feldspars are found in each structural type depending on the mode of occurrences and nature of graphite vein (Touzain *et al.*, 2010). Gangue minerals in graphite are mainly mechanically attached to the graphite surface and some mineral impurities are intercalated between graphene layers. Chemical analysis shows that Fe, Ca, Mg, Si, Al and Na are the abundant trace elements with lesser concentrations of transition metals such as Cu, Ni, Co and Zn (Dissanayake *et al.*, 1988). Recent investigations have revealed that vein graphite in Sri Lanka to be a potential candidate for the anode of lithium-ion rechargeable batteries and its surface modification may increase the performances (Balasooriya *et al.*, 2007). However, they directly used raw graphite without removing impurities before surface modification.

Various thermal and chemical purification methods have been investigated to remove the mechanically attached and intercalated impurities in natural graphite. Thermal treatments include the heating of natural graphite up to 1500 to 2400 °C in an inert environment which is extremely costly (Zaghib *et al.*, 2003). The other purifying method is the chemical treatment where graphite is reacted with mineral acids such as nitric, sulfuric, hydrochloric and hydrofluoric (Shui *et al.*, 2006; Jeongyun and Byounggon, 2007). However, use of strong acids is not a cost effective method. Therefore, this work focuses on investigating the possibility of using low-cost chemical treatment methods for purification of Sri Lankan vein graphite with the aim of using the treated graphite as anode material in lithium-ion rechargeable batteries.

2. Materials and Methods

Natural Sri Lankan vein graphite from Bogala and Kagatagaha-Kolongaha graphite mines were collected for this study. Identification of different structural varieties was done by visual inspection. Small chips from each variety were then crushed in a vibratory disk mill for 3 to 4 minutes to form a powder. Particle size fraction < 53 μm separated by mechanical sieving was used for analysis.

3.75 g of raw graphite was leached in aqueous solutions containing 5, 10, 15, 20, 25 vol.% HCl (25 ml each) separately and heated to 60-65 °C for 75 minutes. The solid was filtered and washed with copious amount of water until the solution pH became neutral (pH 7). This process was carried out by vigorous stirring and vacuum filtering. The acid-leached materials were vacuum dried at 100°C for 15 hours. 3.0 g of the treated graphite was further leached by the same process and dried as before.

Carbon percentages of the treated graphite samples and untreated graphite samples were determined by heat treating at 950 °C for 3 hours in Muffle Furnace, according to ASTM – C 561 and weighing the residues. Each of these samples was vacuum dried at 105 °C for 3 hours to remove moisture before determining the carbon content. Impurity contents of the filtrates (Fe, Cu, Mg and Ca) were determined by Atomic Absorption Spectrophotometer (GBC 932AA).

3. Results and Discussion

The graphs presented in Figure 1 show the effect of HCl concentration on upgrading the carbon content of different structural types of vein graphite from Bogala and Kahatagaha mines. These results suggest a strong dependence of final purity on HCl concentration and the initial purity.

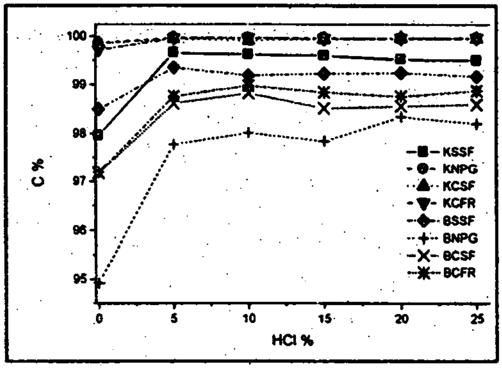

Figure 1 - Effect of HCl concentration on upgrading the carbon content in vein graphite

Bogala shiny-slippery-fibrous (BSSF) graphite and all structural varieties from Kahatagaha mine contain more than 98% carbon. The maximum carbon content of these graphite samples were obtained from the repeated treatment with 5 vol. % HCl. The higher HCl concentrations do not show any significant effect on increasing carbon percentage. Initial carbon content of BSSF graphite was 98.48% and it was upgraded to 99.35% when repeatedly leached in an aqueous solution of 5 vol. % HCl. Kahatagaha shiny-slippery-fibrous (KSSF), Kahatagaha needle-platy graphite (KNPG), Kahatagaha coarse flakes of radial (KCFR) and Kahatagaha coarse striated-flaky graphite (KCSF) contained 97.95%, 99.86%, 99.72% and 99.85% of carbon, respectively. KSSF graphite which has the lowest carbon content in Kahatagaha mine upgraded to 99.66% after repeated treatment with 5 vol.% HCl. Further, the carbon content of KNPG, KCSF and KCFR types increased up to 99.97%, 99.92% and 99.96%, respectively, when repeatedly leached in an aqueous solution of 5 vol. % HCl. This suggests that HCl concentration should be kept at 5 vol. % for the graphite with initial purity greater than 98%.

Bogala coarse striated-flaky graphite (BCSF) and Bogala coarse flakes of radial graphite (BCFR) types from Bogala mine contained 97-97.5% of carbon. The product purity of BCSF and BCFR graphite reached its maximum level 98.82% and 98.97% when repeatedly treated with 10 vol.% HCl. The effect of HCl concentration became insignificant above that concentration. This suggests that HCl concentration should be kept at 10 vol.% for the graphite with initial purity ranging from 97-98% of carbon. The lowest carbon content was present in BNPG and it was 95%. It could be upgraded to 98.27% when leached repeatedly with 20 vol.% aqueous solution of HCl. Figure 2 shows the comparison of the effect of HCl concentration on Fe leaching from graphite into the solution during the first round of treatment.

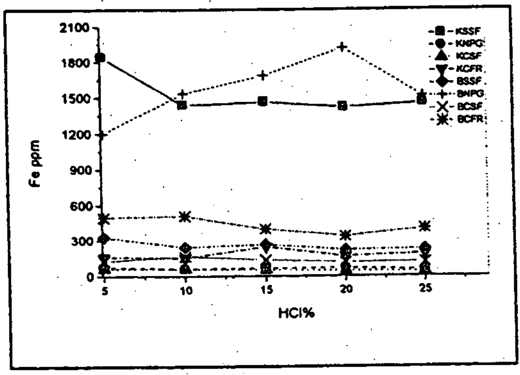

Figure 2 - Effect of HCl concentration on removal of Fe from vein graphite after the first round of treatment

These results show that the pattern of Fe removal is comparable to that of the upgrading of carbon content in each structural type. The highest concentration of Fe removal was observed when raw graphite was treated with 5 vol. % HCl for BSSF, KSSF, KNPG, KCSF, and KCFR where initial carbon contents were higher than 98%. Fe concentrations of filtrate in above samples did not increase with HCl concentration. However, Fe concentration of BCSF and BCFR increased with HCl concentration and reached its maximum when treated with 10 vol. % HCl.

Table 1 - Concentration of impurity in filtrate after the first round of treatment

Structural Type	HCl vol. %	Concentration of Impurity in Filtrate			
		Fe ppm	Cu ppm	Mg ppm	Ca ppm
BSSF	5	328.02	7.17	256.92	125.4
BNPG	20	1920.68	33.04	34.23	15.3
BCSF	10	166.31	0.5	225.12	251.7
BCFR	10	511.35	7.25	135.65	76 4
KSSF	5	1843.39	45.66	16.65	3.79

Table 2 - Concentration of impurity in filtrate after the second round of treatment

Structural Type	HCl vol. %	Concentration of Impurity in Filtrate			
		Fe ppm	Cu ppm	Mg ppm	Ca ppm
BSSF	5	16.62	3.88	2.44	2.17
BNPG	20	110.16	18.44	4.26	5.83
BCSF	10	135.1	1.7	0.83	10.58
BCFR	10	11.89	1.94	0.73	10.7
KSSF	5	57.64	1.72	7.24	4.29

Tables 1 and 2 give the concentrations of Fe, Mg, Ca and Cu in the filtrate after treatments where higher enhancements of carbon percentages were observed. Generally, the concentration of Fe, Ca and Mg in the solution obtained after chemical treatment of Bogala graphite varieties was relatively high compared to that of Kahatagaha, the major exception being KSSF. Gangue minerals such as pyrite, chalcopyrite, calcite and, biotite, which are physically attached to the graphite surface react with HCl releasing Fe, Mg, Ca and Cu into the solutions. Concentrations of impurity in the filtrate during the second round of treatment were significantly reduced compared to those of the first round of treatment, indicating the effectiveness of purification process.

4. Conclusions

This study revealed that the impurities in Sri Lankan vein graphite can be effectively removed by treating with 5 - 20 vol..% HCl solutions at 60 - 65 °C depending on initial purity of different structural varieties. This method uses mineral acids with low concentrations at low temperature compared to the previous methods (Zaghib, 2003; Jeongyun and Byounggon, 2007). It is well known that the electrochemical characteristics of anode material are greatly degraded by the presence of impurities. Therefore, this modified purification method can be successfully used to enhance the Sri Lankan vein graphite making them suitable for the anode of lithium ion rechargeable batteries.

5. Acknowledgements

Financial assistance by the Human Resources Development (HRD) program of the Higher Education for Twenty First Century (HETC) project of Ministry of Higher Education is acknowledged.

6. References

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