

Development of Lithium Ion Rechargeable Batteries by Using Sri Lankan Graphite and Locally Synthesized Low-Cost Materials

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Introduction

Lithium-ion battery (LIB) is a family of rechargeable battery types in which the lithium ions move from the negative electrode to the positive electrode through the electrolyte. LIBs are currently one of the most popular types of battery for portable electronics with one of the best energy-to-weight ratios, no memory effect and a slow loss of charge when not in use. However, the present generation of LIBs has many limitations, such as high internal resistance, expensiveness, temperature effect, aging effect, short circuiting, environment effect and over heating. The present inferior electrode materials are the main reason for these drawbacks and hence the main obstacle to achieve reliable and cheaper lithium-ion batteries (Pushpaka *et al.*, 2008).

This abstract presents a study of developing $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ based cathode electrodes and $\text{NiO-LiFeO}_2\text{-LiCoO}_2$ based anode electrodes with the Sri Lankan graphite as electrical conductivity enhancer. These novel electrode materials were synthesized by using Glycine-nitrate and Pechini methods, which are low cost techniques but can result in powders with high purity, homogeneity and particle morphology that are highly desired for LIB electrodes (Wijayasinghe *et al.*, 2006).

On the other hand, the expensive synthetic carbon materials are now being used as electrical conductivity enhancer of LIB electrodes, currently. In a recent research work on Sri Lankan graphite at the Uva Wellassa University with the collaboration of Institute of Fundamental Studies our group indicated of having sufficient electrical conductivity in Sri Lankan graphite to be used as conductivity enhancer (Geethika *et al.*, 2010). Sri Lanka has been well known for processing high purity graphite, which is mainly being exported as cheap raw materials. Introducing this cheaper material for the high-tech energy conversion devices will definitely reduce the cost of these devices while also adding value to our mineral resources. By considering these factors, Sri Lankan Bogala graphite was investigated in this study as a conductivity enhancer in LIB electrodes.

Methodology

Two wet-chemical powder synthesis techniques, Glycine-nitrate and Pechini methods, were employed to prepare the novel electrode materials. Metal Nitrates, LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ of analysis grade were used as starting materials with the organic precursor solutions of citric acid, Glycine and ethylene glycol.

In the Pechini method, powders were prepared with ethylene glycol to citric acid ratio of 1:4. In the Glycine-nitrate method powders were prepared by keeping glycine:nitrate ratio as 0.6:1. Subsequently powders were calcined at 900 °C in static air in a box furnace. The calcined powders were pressed in to green pellets of 12mm in diameter, followed by sintering at 1000 °C in a horizontal tube furnace in static air. The electrical properties of the selected materials were determined by using d.c. four-probe techniques. Specimens for measuring d.c four-probe conductivity were prepared by coating both end surfaces of the pellet with gold paste to provide better contact with the electrodes of the sample holder.

Fabrication of solid flexible electrodes from the selected materials was done via tape casting.

Bellcore-type electrodes of about 0.1 mm thickness and 10 mm diameter, were prepared for electrical measurements by mixing the electrode material with PvdF-HFP (KynarFlex 2801), a carbon source in proportions 1:0.25:0.10 by weight. Those proportions mixed and blended with propylene Carbonate (PC, Merck) Corresponding to 40% of active material weighted and dissolved with acetone. As the carbon sources for enhancing conductivity, Sri Lankan graphite samples obtained from Bogala mines were investigated. To compare their performance, synthetic graphite was used as a reference material. The details of the selected graphite samples are given in Table 1. In order to measure the electrical conductivity of these selected Sri Lankan graphite and synthetic graphite, the DC four Probe measurements were performed on the pellets prepared by these samples.

Table 1: Selected Sri Lankan Bogala graphite samples for conductivity enhancing in LIB electrodes

Sample	Position	Grade	Carbon%
BA	BR Mill	BP 8085	80-85
BB	Micron Mill	BFPH 99	99
BC		BFP 9799	97-99

Solid flexible tapes were prepared by using these selected cheaper local graphite by replacing expensive synthetic graphite and changing the proportion of other chemicals. The electrical conductivity of the prepared solid flexible electrodes was measured by employing the vander Paw method at room temperature. For these fabrication and characterization, a manual tape caster and a vander Paw measuring setup designed and constructed under this project work.

Results and discussion

Under the powder synthesis work, LiCoO_2 , LiFeO_2 , and some other novel oxides powders were prepared. The details of these prepared novel compositions are given in Table 2 and Table 3. The measured room temperature d.c electrical conductivity of the synthetic graphite used as a reference material for this study was 1.43×10^2 S/cm. In comparison, the measured room temperature conductivities of Sri Lankan BA, BB, and BC-Bogala graphite were 0.80×10^2 S/cm, 1.15×10^2 S/cm and 1.37×10^2 S/cm, respectively. This reveals that the conductivities of these selected Sri Lankan graphites are almost close to that of the synthetic graphite, which is the state of the art conductivity enhancer of LIB electrodes.

Of the solid flexible cathode electrodes prepared with the expensive synthetic graphite as a reference materials, the room temperature electrical conductivity of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.22}\text{Fe}_{0.11})\text{O}_2$ electrodes were 10.9×10^2 S/cm and 15.8×10^2 S/cm, respectively. Very interestingly, as seen in Table 2, the cathode electrodes prepared with the same electrode materials but by using cheaper local graphite added electrode also show of having comparable electrical conductivities

Furthermore, the room temperature electrical conductivity of 63.75% $\text{NiO} + 11.25\% \text{LiFeO}_2 + 15\% \text{LiCoO}_2$ anode electrode which prepared by using expensive synthetic graphite was 14.63×10^2 S/cm. Interestingly as seen in Table 3., the local graphite added electrode of the same material composition shows of having sufficient electrical conductivity.

Table 2: The electrical conductivity of cathode electrodes developed by using Sri Lankan graphite

Electrode materials for cathodes	Sri Lankan Bogala graphite/ grade	Conductivity (S/cm) at 25 °C
Li(Ni _{1/3} Mn _{1/3} Co _{1/3})O ₂	BA/BP8085	6.00 × 10 ²
Li(Ni _{1/3} Mn _{1/3} Co _{1/3})O ₂	BB/BFPH99	3.61 × 10 ²
Li(Ni _{0.33} Mn _{0.33} Co _{0.22} Fe _{0.11})O ₂	BB/BFP9799	6.88 × 10 ²

Table 3: The electrical conductivity of anode electrodes developed by using Sri Lankan graphite

Electrode materials for anode	Sri Lankan Bogala graphite/grade	Conductivity (S/cm) at 25 °C
63.75% NiO+11.25%LiFeO ₂ +15% LiCoO ₂	BA/BP8085	1.86×10 ²

As it is stated elsewhere (Pushpaka *et al.*, 2008) in order to get the optimum performance, the LIB electrodes should possess an electrical conductivity of the order 10² S/cm at room temperature. In the light of this, all the electrodes developed in this study with locally synthesized low-cost materials and cheaper Sri Lankan graphite show all most similar electrical performance as of the expensive state of the art electrode system of present day Lithium-ion batteries.

Conclusions

The electrical conductivity of the Sri Lankan graphite selected for this study shows of having appropriate conductivity to be used as a conductivity enhancer in electrodes. Further, this study revealed the possibility of fabricating solid flexible electrodes with the locally synthesized novel oxides using low-cost synthesis techniques. The electrical performance of the electrodes prepared with the cheaper local graphite are almost comparable with those prepared with expensive synthetic graphite, which is the state of the art conductivity enhancer of LIB electrodes. As a whole this study indicates the possibility of preparing cheaper electrodes for LIB with locally synthesized low-cost materials and Sri Lankan graphite.

References

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