

Polymer Graphite Composite as Anodes for Li-ion Batteries

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Introduction

To ensure long cycle life and safety, different types of carbons including graphite and coke have been studied as anodes for the Li-ion battery. In theory, graphite can intercalate with lithium upto the ratio 1:6, forming the compound LiC_6 , with a capacity of 372 mAh/g. However, carbon anodes that are used currently have substantially lower capacity than LiC_6 . Also, graphite anodes exhibit capacity loss between the first discharge and the first charge. This is due to the irreversible reactions that take place with lithium. In commercial Li-ion cells this loss in capacity is compensated with the use of excess cathode material. This, however, leads to the decrease in specific energy density and thus an increase in the cell cost.

Recently, attempts were made to suppress the irreversible solvated lithium intercalation into graphite by modifying the electrolyte¹ and/or to the electrode material². However, these modifications do not decrease the irreversible capacity satisfactorily and also lead to an increase in the deadweight of the battery, thus resulting in the reduction of the reversible capacity.

In this work, modification using polymer has been carried out as a method to reduce the irreversible capacity of graphite. The modification with the polymer serves in the reduction of the irreversible capacity. Polypyrrole has already been tried as a conducting polymer in the case of cathodes like Manganese dioxide,³ wherein it has been tried as a replacement to the conducting additives like Carbon conductors, in addition to serving as the binder. Thus, Polypyrrole has been used in cathodes to couple the characteristics of a binder and a conductor, reducing the deadweight in the electrode. However, in this work, addition of Polypyrrole leads to superior graphite anodes with a lower irreversible capacity and good cycle life. The polymer also serves the dual purpose of a binder and a conductor, thus reducing the deadweight of the electrode.

The objective of this work is to develop a superior carbon (graphite) anode for Li-ion cells by a modification treatment based on the polymerization of conducting polymers. Polypyrrole is formed in aqueous solution over graphite hosts, which could result in a combination that has the favorable characteristics of a low irreversible capacity, while retaining the reversible capacity.

Experimental

Pyrrole was polymerized in an aqueous solution containing the graphite particles. Sodium salt of dodecyl benzene sulfonic acid was used as a dopant. Monomer was slowly added into the aqueous slurry of DBSNa/graphite at 0°C for 40 hrs. The resultant powder was thoroughly washed with water and methanol several times and then dried in vacuum oven.

Pellets with the composite material were prepared by cold rolling technique. Disc electrodes of area of 1.4 cm² were cut out from the cold pressed material.

Electrochemical characterization studies were performed using a three electrode T-cell set up. Pure lithium was used as the counter and reference electrode. 1M LiPF_6 was used as the electrolyte in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC).

Results and Discussion

Charge-discharge characteristics of the samples were studied by cycling the samples between 2V and 0.005 V at C/15 rate. Fig 1 shows the first cycle charge-discharge characteristics of the polymerized sample of SFG10 graphite. The charge-discharge curve of the bare graphite is shown for comparison. The figure shows a significant decrease in irreversible capacity in the case of polymerized composite electrode. The bare graphite has an irreversible capacity of 234 mAh/g, while in the case of the polymer composite electrode, the irreversible capacity is reduced to the extent of 96 mAh/g. Thus, the polymerized composite leads to a recovery of about 138 mAh/g of irreversible capacity. Also, there is negligible decrease in the reversible capacity (~4 mAh/g) of the composite electrode as compared to that of the virgin graphite electrode.

CVs were carried out to understand the mass transfer limited processes occurring in polymer composite and bare SFG 10 electrodes. The CVs of the composite electrode indicates a significant reduction in the lithium solvation reaction. A steady state Impedance Model was used to calculate the diffusion co-efficient of lithium intercalation in case of tin encapsulated and bare SFG 10 graphites. EIS data at low frequency range was used for this purpose. Finally, charge-discharge characteristics, conductivity data, rate capability, cycle life studies show polymer-graphite composite materials to be promising candidates for Li-ion battery applications.

Acknowledgment

The authors acknowledge financial support in part by the DOE Division of Chemical Sciences, Office of Basic Energy Sciences.

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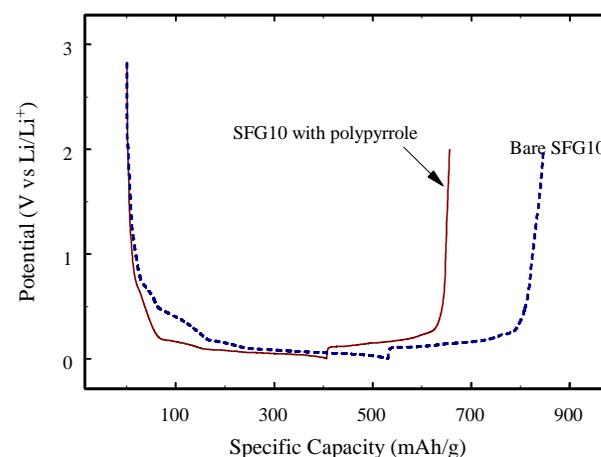


Fig.1. First cycle charge-discharge characteristics of SFG10 samples