SAND2000-2843C

Synthesis and Characterization of Sn-Coated SFG10 Graphites as Negative Electrodes in Li-Ion Cells

B. Veeraraghavan A. Durairajan, R.E. White, B. N. Popov
Department of Chemical Engineering
University of South Carolina
Columbia, SC 29208
and
Ronald Guidotti
Sandia National Laboratories
Albuquerque, NM 87185-0614

ABSTRACT

A Sn-coating study was undertaken with a commercial graphite, Timcal SFG10, using an electroless deposition process. The purpose of the work was to increase the reversible capacity and reduce the irreversible losses associated with this material when used as a negative electrode in Li-ion cells. The electrochemical performance of the Sn/C composite materials was improved over that for the bare (uncoated) graphite up to a Sn level of 15% when tested at rates between C/15 and 2C. The overall irreversible losses were greatly reduced under the same conditions. Corroboration of the improved performance was obtained through cyclic voltammetric experiments and by complex-impedance spectroscopy.

INTRODUCTION

Lithium ion batteries are in great demand as the high energy density power sources. Lithium batteries started to come into existence when the search for inorganic materials, which could incorporate lithium ions into their structure without significant change in their host structure, yielded some promising results. The first batteries that were made, used chalcogenides that exhibited a layered cadmium-iodide type structure.[1] These early prototypes used lithium metal as the anode. This arrangement lead to serious safety problems as metallic dendrites were formed on the anode during cycling. To overcome this problem, "rocking-chair" type secondary lithium batteries were produced which used lithium metal oxide as the anode and a carbon compound as the anode.

To ensure long cycle life and safety, different types of carbon including graphite[2] and coke[3] have been studied for the battery anode. In theory, graphite can intercalate with lithium up to the ratio 1:6, forming the compound LiC_6. The theoretical capacity arising out of this intercalation compound is 372 mAh/g of carbon.[4] However, commercial cells are now using anodes which realize substantially lower capacity than LiC_6. The other main problem associated with the use of graphite is the loss in capacity between the first discharge and the first charge. This is due to the irreversible reactions that take place during the first intercalation involving reduction of solvent and electrolyte. Part of the Li is incorporated into a protective solid electrolyte interface (SEI). This SEI layer limits the electrochemical reduction of solvent and electrolyte while allowing Li-ion transport during charge and discharge. In commercial Li-ion cells, this resulting loss in capacity is

compensated by the use of excess cathode material. This, however, leads to the decrease in specific energy density and thus an increase in the cell cost.[5,6] These irreversible reactions can also cause gas evolution, which may result in some very serious safety issues, such as cell can buckling, cell venting, electrolyte spillage and even fire.[5,7]

Recently, some attempts to suppress the irreversible solvated lithium intercalation into graphite have been made by adding inorganic agents such as CO_2,[8] NO_2[9] and SO_2,[10] or organic agents such as crown ethers to the electrolyte.[11,12] These additives contribute to the formation of a less permeable SEI film, which effectively decreases the diffusion of solvated lithium ions through the surface of the graphite, but these additives still induce some irreversible capacity in the first cycle because they also react with intercalated lithium. Another novel approach has been to coat graphite with metals like Ni,[13] to reduce the lithium solvation reaction, thereby reducing irreversible capacity. The problems associated with such an approach is that the metal does not contribute to cycling, thereby reducing specific capacity of the material.

Tin-based Li-storage materials are being considered as the most promising replacement of carbonaceous anodes in Li-ion batteries. Lithium alloys extensively with tin, up to a stoichiometry of $Li_{22}Sn_5$,[14] which corresponds to a specific capacity of 991 mAh/g of Sn. However, Sn, when used as anode material loses capacity rapidly. The reason for this is that Sn expands as much as 259% when lithium is inserted.[15] During cycling, this large expansion and contraction associated with intercalation and deintercalation of Li^+ ions leads to disintegration of the anode material, thereby reducing the capacity and resulting in poor cycle life in applications. It has been suggested that reducing the particle size of the Li^+ storage material may improve the situation. Tin, in the form of a composite oxide shows very good cyclability compared to that of pure Sn or Sn alloys. This is attributed to the presence of Sn as finely divided particles and the composition which prevents the aggregation of Sn.[16] The objective of this work is to develop superior carbon (graphite) anodes for Li-ion cells by a surface modification treatment based on electrocatalytic inclusion of nanostructured Sn in Li-ion storage materials. Tin is coated over graphite hosts, which could result in a combination that has the favorable properties of both materials. This combination, when optimized, should provide improvements over material designs that are based on the use of one or more inactive phases to restrain the pulverization of the Li-Sn alloy system during charge and discharge reactions.

EXPERIMENTAL

To study the effect of tin, synthetic graphite, commercially known as SFG10, was used as received from the Timcal Corporation. Nanostructures of tin was embedded on carbon surface using an in-house developed one-step electroless-electrocatalytic process. The carbon material was pretreated in a reducing hypophosphite bath and depositions were carried out from a bath containing the desired metal ions. Next the metal-carbon composite particles were thoroughly washed in distilled water and were dried in vacuum at 200°C for 24 h.

Pellets of the finely ground metal encapsulated carbon samples were prepared by cold-rolling technique. Polytetrafluoroethylene (PTFE) (10wt%) was used as a binder in all the cases. Disk electrodes 1.4 cm^2 in area were cut out from the cold pressed material. Electrochemical characterization studies were performed using a three electrode T-cell set up based on a ½" perfluoroalkoxy tee (Swagelok). T-cells were prepared in a glove box filled with ultra pure argon (National Gas and Welders Inc). The electrodes in the T-cells were prepared by cold pressing material on both sides of metal current collectors (304 SS cylinders). Pure lithium metal 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). Whatman fiber membrane (Baxter Diagnostic Co.) was used as a separator.

Cyclic voltammograms (CVs) were obtained using a scan rate of 1 mV/s using EG&G potentiostat (Model 273A). The charge-discharge behavior of each cell was investigated under galvanostatic conditions using an Arbin Battery Test Station (BT-2043) at a current of 0.5 mA (C/3 rate). The rate capability studies were performed using the Arbin Battery Test Station (BT-2043) at various rates. The complex-impedance analyses were performed using a Solartron 1255 analyzer along with EG&G potentiostat (Model 273A) over a frequency range of 65 kHz to 100 mHz with a signal amplitude of 5 mV peak to peak.

RESULTS AND DISCUSSION

The effect of tin on SFG10 graphite was studied using charge-discharge studies. The samples were cycled between limits of 5mV for discharge and 2V for charge. The charge-discharge studies were performed at a C/3 rate. Here, the discharge capacity refers to the lithium intercalation capacity and the charge capacity is referred as the lithium de-intercalation capacity. Figure 1 shows the charge-discharge curves for bare and Sn-coated SFG10 graphites for the first cycle. Figure 2 shows the charge discharge curves for bare and Sn-coated SFG10 graphite for the second cycle. The capacities are reported with respect to per gram of the active material used (graphite+Sn). From Figure 2, it is evident that addition of Sn improves the reversible capacity of the samples. As the Sn content on the graphite increases, the reversible capacity also increases up to a Sn composition of 15%. It is also seen that at 20% Sn, the reversible capacity starts to decrease. Table 1 gives the values of the percentage increase in reversible capacity as a function of of Sn content. Figure 3 shows the percentage increase in the reversible capacity as a function of the Sn content in the sample. From the graph, it is apparent that the optimum Sn content is 15%, after which the reversible capacity starts to drop off. Table 1 also gives the percentage of irreversible capacity in each sample, which is calculated by the relative difference between the 1st cycle discharge capacity and the 2nd cycle discharge capacity, whose values are also tabulated in Table 1. It is clearly seen from the table that the percentage of irreversible capacity decreases when Sn is added to the graphite, plateauing near 36.6% when the Sn content reaches 15%.

CVs were obtained to understand the reactions that are happening in the Sn-coated samples. Figure 4 shows the second-cycle CV obtained for the 15%-Sn sample, since it has been chosen as the optimum composition. The CV of bare graphite is shown for comparison. The CVs were obtained by sweeping the potential from 3 V up to 0.01 in the cathodic direction and back to 3 V in the anodic direction at a scan rate of 1 mV/s. From the CVs it is seen that the peak currents and area of the curve increase for the Sn-coated sample, which supports the increase in reversible capacity observed during charge-discharge studies. However, no new peak was observed that can be assigned to the reaction of Sn with Li, which shows that the reaction occurs at the same potential range as the lithium intercalation into graphite for these experimental conditions.

Figure 5 shows the complex-impedance spectra of the bare and Sn-coated SFG10 samples. The graph clearly shows the decrease in polarization resistance (smaller charge-transfer semicircle), as the content of Sn increases. Sn, being a good electronic conductor, decreases the resistance. It also reduces the amount of SEI layer, which contributes to the reduction in the polarization resistance of the Sn-coated samples.

The relative rate capabilities of the bare graphite and the 15%-Sn coated graphite are shown in Figure 6 for rates of C/15, C/6, C/3, C and 2C. The bare graphite gives 84% of the theoretical capacity (313 mAh/g) when a very low rate of C/15 is used. As the rate is increased the useful capacity that can be drawn out of the sample also drops, and reaches a value of 17.5% of the theoretical capacity (65.2 mAh/g) at a 2C rate. Table 2 gives the value of the reversible capacities of bare and 15% Sn-coated SFG10 graphite at various discharging rates.

CONCLUSIONS

Sn coatings were incorporated into a commercial graphite, Timcal SFG10, by an electroless reduction process to form Sn/C composites suitable for use a negative electrodes in Li-ion cells. At levels up to 15% Sn, the reversible capacities of the composites during galvanostatic cycling are significantly increased relative to the bare graphite for C rates of C/15 to 2C. At a C/3 rate, a reversible capacity of 260 mAh/g is obtained at 15% Sn, compared to 128 mAh/g for the uncoated graphite, an increase of over 103%. The irreversible capacities are also reduced for the Sn-coated graphites, dropping from 45.3% for the uncoated graphite to 36.6% for Sn levels of 15% to 20%. Cyclic voltammetric experiments corroborated the galvanostatic cycling tests, with Sn-coated graphites showing higher peak currents and capacities relative to the uncoated control material. Additional corroboration was obtained through complex-impedance spectroscopy. Coating of the graphite with Sn reduces the charge-transfer resistance and overall polarization, very likely by reducing the amount of SEI formation.

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support in part by the Dept. of Energy Division of Chemical Sciences, Office of Basic Energy Sciences and Sandia National Laboratories, Albuquerque, NM.

(Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin company, for the United States Department of Energy under Contract DE-AC04-94AL85000.)

REFERENCES

1. M. S. Whittingham, *Science,* **192**, 1126 (1976).
2. M. B. Armand, *Material for Advanced Batteries*, D.W. Murphy, J. Broadhead and B. C. Steele, editors, p. 145, Plenum press, New York (1980).
3. D. Guymard and J. M. Tarascon, *J. Electrochem Soc.*, **139**, 937 (1992).
4. T. Zheng, Q. Zhong, and J. R. Dahn, *J. Electrochem Soc.,* **142**, L211 (1995).

5. P. Arora, R. E. White and M. Doyle, *J. Electrochem. Soc.*, **145**, 3647 (1998).

6. W. Xing and J. R. Dahn, *J. Electrochem. Soc.*, **144**, 1195 (1997).
7. T. Osaka, T. Momma, Y. Matsumoto, Y. Uchida, *J. Electrochem. Soc.*, **144**, 1709 (1997).
8. Y. Ein-Eli, S. R. Thomas and V.R. Koch, *J. Electrochem. Soc.*, **143,** L195 (1996).
9. O. Chusid, Y. Ein-Eli, and D. Aurbach, *J. Power Sources,* **43-44**, 47 (1993).
10. J. O. Besenhard, M. W. Wagner, A. D. Jannakoudakis, P. D. Jannakoudakis, and E. Theodoridou, *J. Power Sources,* **43-44**, 413 (1993).
11. Z. Ogumi, M. Inaba, Y. Kawatate, A. Funabiki, and T. Abe, Abstract 73, *The Electrochemical Society Meeting Abstracts,* San Diego, May 3-8, 1998.
12. Z.X. Shu, R.S. McMillan, J.J. Murrary and J. Davidson, *J. Electrochem. Soc.*, **142,** L161 (1995).
13. P. Yu, J. A. Ritter, R. E. White and B. N. Popov, *J. Electrochem. Soc.*, **147**, 1280, (2000).
14. J. Wang, I.D. Raistrick, R.A. Huggins, *J. Electrochem. Soc.*, **133,** 457 (1986).

15. I.A. Courtney, J.R.Dahn, *J. Electrochem. Soc.*, **144**, 2045 (1997).
16. J.Y. Lee, R. Zhang and Z. Liu, *J. Power Sources,* **90**, 70-75 (2000).

List of Figures:

TABLE 1. Comparison of increase in reversible capacities in tin coated samples as compared to bare graphite material (SFG10)

Electrode	**Reversible capacity[1](mAh/g)**	**Increase in reversible capacity[2] (%)**	**1st cycle discharge capacity(mAh/g)**	**Irreversible Capacity[3] (%)**
Bare SFG10	128.1	-	234.1	45.27
5% Sn-coated SFG10	152.1	18.71	270.1	43.70
10% Sn-coated SFG10	253.8	98.08	407.7	37.75
15% Sn-coated SFG10	260.3	103.18	410.9	36.64
20% Sn-coated SFG10	238.7	86.34	376.6	36.61

TABLE 2. Rate-capability data for the SFG10 samples.

Sample	**Reversible capacity of the sample (mAh/g)**				
	C/15	**C/6**	**C/3**	**C**	**2C**
Bare	313.0	226.3	128.1	89.1	65.2
15% Sn	427.7	336.6	260.3	189.1	144.6

---

[1] Reversible capacity =2nd cycle discharge capacity

[2] Increase in Reversible Capacity =(2nd cycle discharge capacity of coated sample-2nd cycle discharge capacity of bare sample) /2nd cycle discharge capacity of bare sample*100

[3] Irreversible Capacity =(1at cycle discharge capacity of sample-2nd cycle discharge capacity of sample) /1st cycle discharge capacity of sample*100

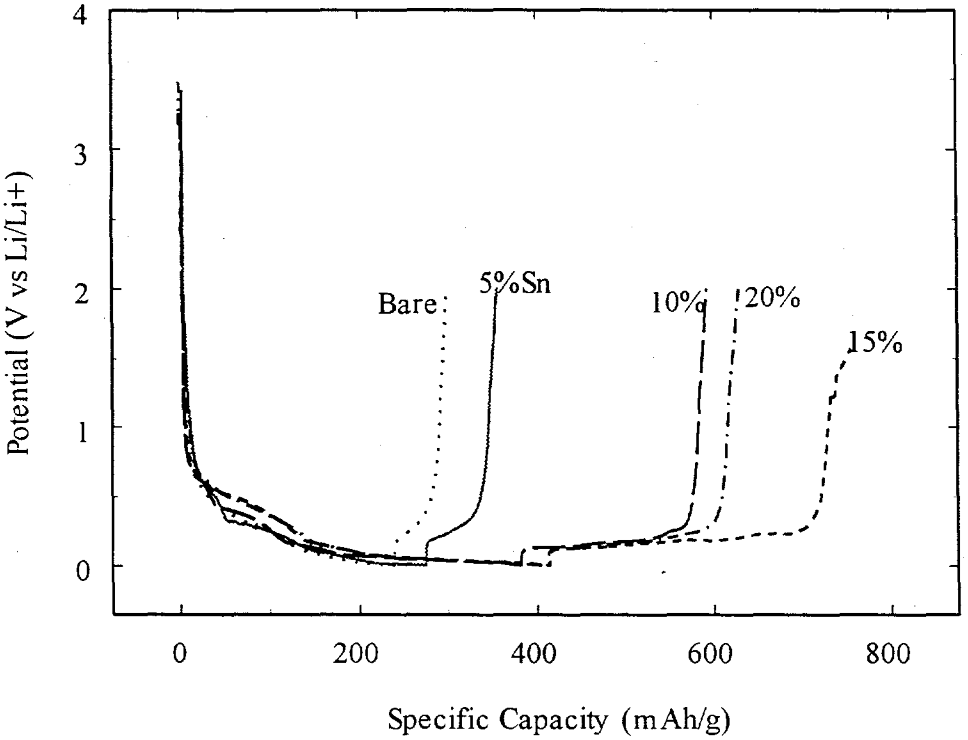

Figure 1. Charge-discharge curves of bare and Sn-coated SFG10 samples for the first cycle at C/3 rate.

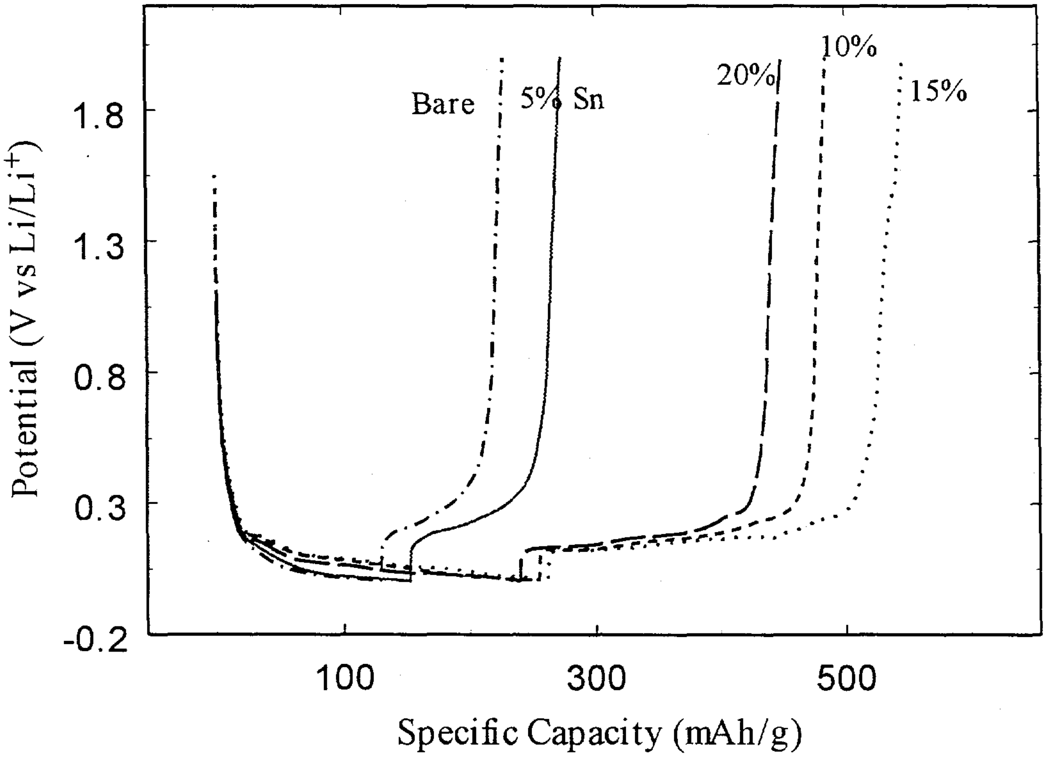

Figure 2. Charge-discharge curves of bare and Sn-coated SFG10 samples for the second cycle at C/3 rate.

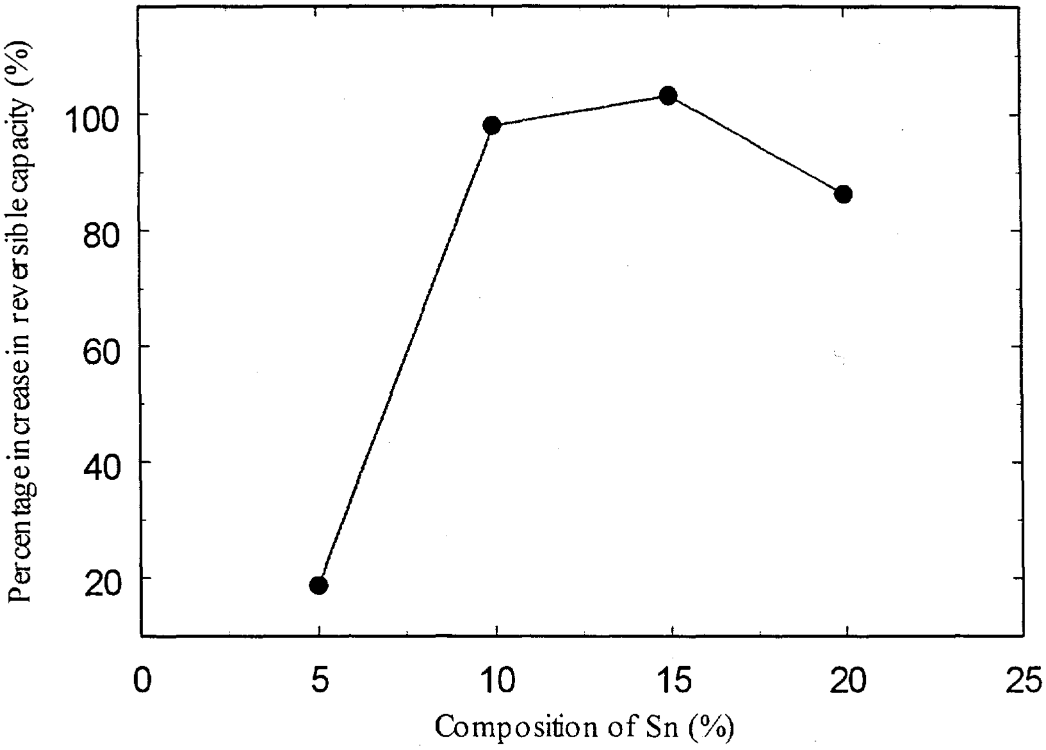

Figure 3. Percentage increase in reversible capacity as a function of composition of Sn.

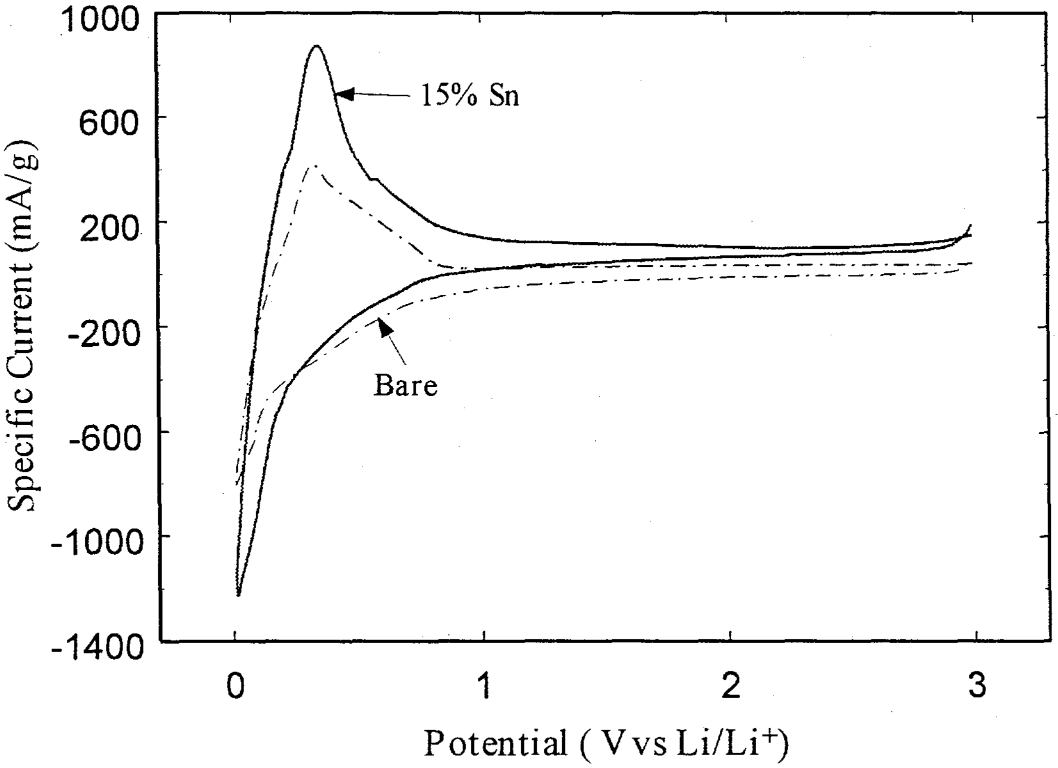

Figure 4. Cyclic Voltammograms of SFG10 samples for the reversible cycle at 1mV/s.

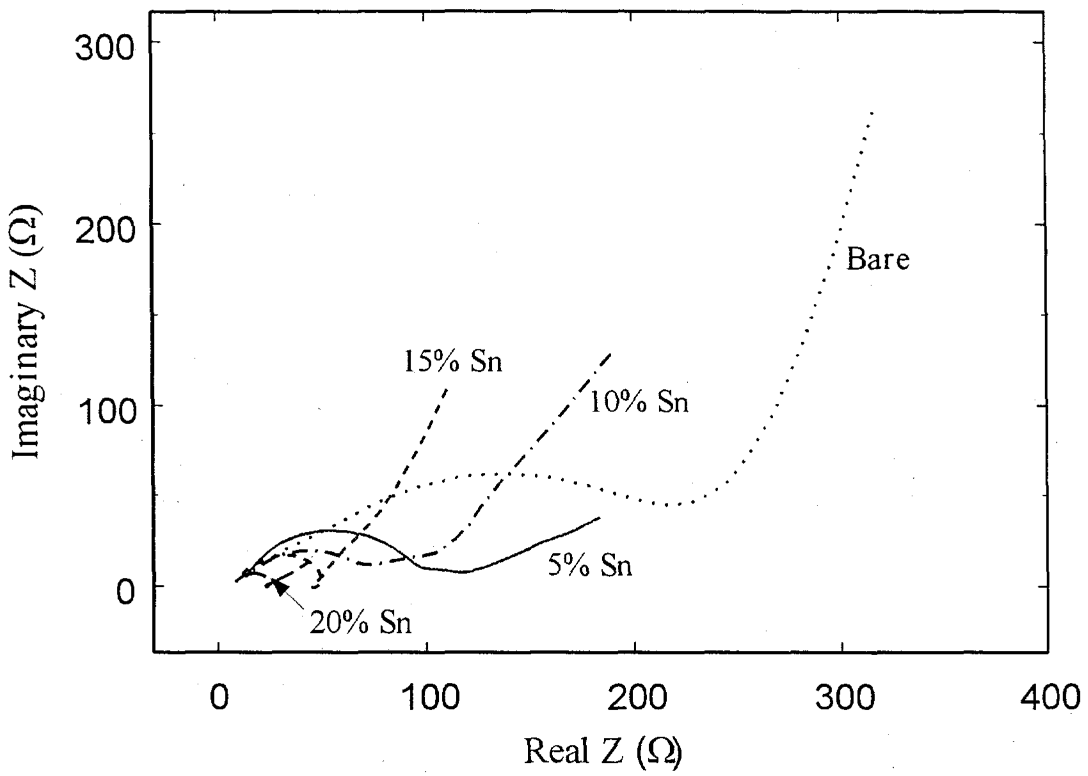

Figure 5. Impedance plots for the bare and Sn-coated SFG10 samples at fully discharged state.

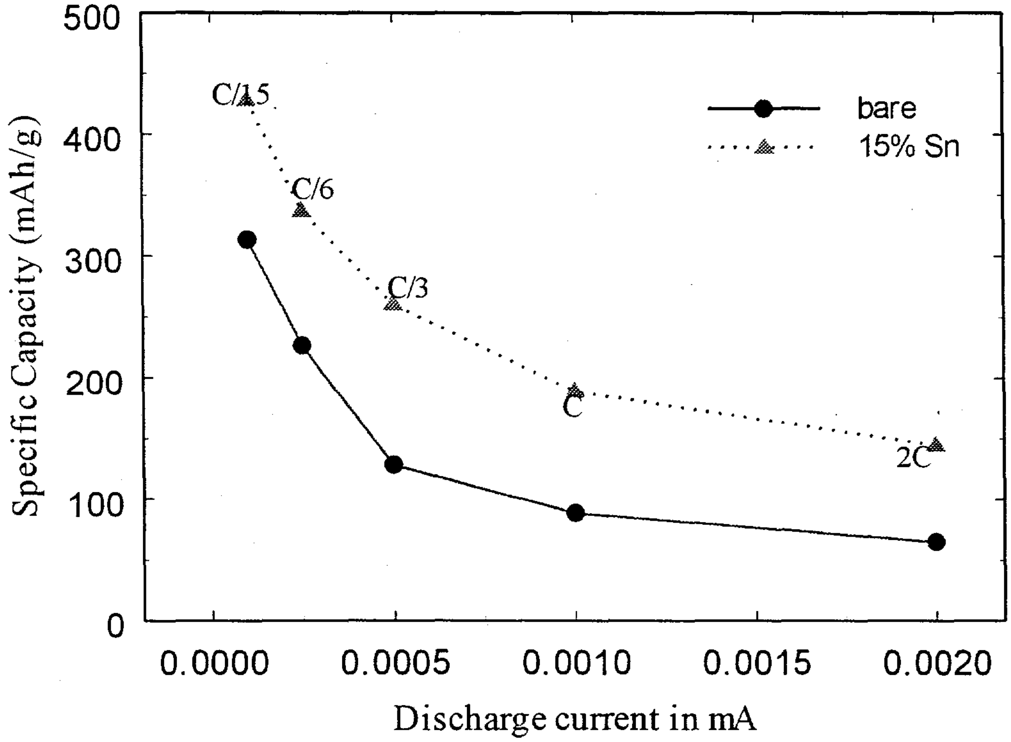

Figure 6. Rate Capability studies of SFG10 samples.