Low hydrogen containing amorphous carbon films—Growth and electrochemical properties as lithium battery anodes

V. Subramanian[a], Tansel Karabacak[b], Charan Masarapu[a], Ranganath Teki[c], Toh-Ming Lu[d], Bingqing Wei[a,*]

[a] Department of Mechanical Engineering, University of Delaware, 130 Academy Street, Newark, DE 19716, United States
[b] Department of Applied Science, University of Arkansas at Little Rock, 2801 South University Avenue, Little Rock, AR 72204, United States
[c] Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States
[d] Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

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ABSTRACT

Amorphous carbon films were deposited successfully on Cu foils by DC magnetron sputtering technique. Electrochemical performance of the film as lithium battery anode was evaluated across Li metal at 0.2 C rate in a non-aqueous electrolyte. The discharge curves showed unusually low irreversible capacity in the first cycle with a reversible capacity of $\sim$810 mAh g^{-1}, which is at least 2 times higher than that of graphitic carbon. For the first time we report here an amorphous carbon showing such a high reversibility in the first cycle, which is very much limited to the graphitic carbon. The deposited films were extensively characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and step profilometer for the structural and surface properties. The hydrogen content of the synthesized films was studied using residual gas analysis (RGA). The low hydrogen content and the low specific surface area of the synthesized amorphous carbon film are considered responsible for such a high first cycle columbic efficiency. The growth mechanism and the reasons for enhanced electrochemical performance of the carbon films are discussed.

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1. Introduction

Increasing demand for compact and light-weight power sources with high energy and power densities from consumer electronics has triggered the search for alternate materials for use as intercalation hosts in lithium ion batteries [1,2]. Both carbonaceous [3] and metal oxide-based [4] materials are under close scrutiny for use as anode materials in lithium ion batteries. Carbon materials used for Li-ion batteries can be broadly classified as graphitic and non-graphitic or soft and hard carbons, respectively [3]. This is mainly based on the possibility to graphitize the carbon by heat treatment, wherein, there is a marked change in the microstructure between the two types of carbons. In general, the graphitic carbon is more ordered with well-organized graphene sheets while the non-graphitic or hard carbon exhibits a high turbostatic disorder [3]. These structural properties of the two types of carbon reflect different lithium insertion and deinsertion properties. The reversible storage of lithium ions is better in graphitic carbon, whereas the overall storage capacity is much higher for the disordered carbon.

The lower specific capacity offered by the graphitic carbon and the higher irreversible capacity in the first cycle for the non-graphitic carbon has sought the attention of the research community to seek for a viable intermediate overcoming the above mentioned disadvantages of these two types of carbon.

Lithium topotactic reactions in graphitic carbon exhibit a staging mechanism during the lithium insertion and deinsertion phenomena [5]. Since the specific surface area of the graphitic carbon is in the orders of a few square meters per gram, the surface film formation reaction is pretty much limited in the first lithium insertion cycle leading to a lower irreversible capacity. In contrast, the amorphous or disordered carbon exhibits a very high specific surface area with lots of pores leading to a very high first cycle irreversible capacity, but with a much higher reversible capacity than the graphitic carbon [6–8]. The main reasons for such a behavior are attributed to the porous nature of the amorphous carbon and the temperature of preparation of the disordered carbon, which in turn determines the hydrogen content of the prepared carbon. In general, carbon materials with high surface area and hydrogen content exhibit large irreversible capacity. In the case of the graphitic carbon the high synthesis temperature prevents the incorporation of any hydrogen that might additionally contribute to the irreversible capacity.

* Corresponding author. Tel.: +1 302 831 6438; fax: +1 302 831 3619.
E-mail address: weib@udel.edu (B. Wei).

The graphitic carbon and its topotactic reaction with lithium have been well studied [5]; however, the electrochemical insertion reactions for lithium in non-graphitic carbon have not been well understood. Dahn and his group have studied extensively the electrochemical behavior of pyrolytic carbon and have established hypothetical models for the reversible and irreversible lithium storage [6–8]. It is pertinent from the earlier studies that both reversible and irreversible capacities of non-graphitic carbon materials are much larger than that of the graphitic carbon. Hence, the ideal material of choice would be a carbon material with minimal first cycle irreversible capacity in conjunction with a reversible specific capacity more than that of graphitic carbon.

Apart from the higher specific capacity of the disordered carbon, another advantage is its flexible synthesis conditions [9]. Since there is no graphitization limitation on the structure, the synthesis of carbon materials at relatively lower temperatures is possible, which is advantageous when direct deposition or synthesis of carbon materials on substrates is envisaged. Various thin film deposition techniques are currently used for the preparation of both metal oxide and carbon-based electrodes for Li-ion batteries [10]. These are particularly interesting when envisaged for microbattery applications where both the anode and cathode are fabricated as thin films [10]. In this paper, we report the DC magnetron sputtering deposition of amorphous carbon (a-C) films directly deposited on current collector Cu foils and their electrochemical properties as Li-ion battery anode.

2. Experimental

Flat carbon film samples were deposited using a DC magnetron sputter deposition system. Films were deposited on circular Cu foils of 1.59 cm diameter, which were placed about 18 cm away from a carbon sputter target (source) of 3 in. diameter and 99.99% purity. The base pressure of 3.0×10^{-7} Torr was achieved by a turbo-molecular pump backed with a mechanical pump. Argon plasma was initiated at a power of 400 W, with the gas flow rate and working pressure of 2 sccm and 2.5 mTorr, respectively. A shutter was placed in front of the Cu foil samples for the first 5 min during the pre-sputter cleaning of the target surface. Samples were then deposited with carbon film for 60–360 min. The maximum temperature of the substrate during the deposition was measured to be about 85 °C using a K-type thermocouple.

The deposited films were studied for their structural and morphological aspects using scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM), and step profilometer for the thickness of the films. The SEM studies on the carbon film deposited on Cu foil were performed using a JEOL-7400. The Cu foil was imaged sideways to estimate the thickness of the carbon film.

AFM analysis was performed with a Park Scientific Autoprobe CP, wherein both the bare Cu foil and the deposited C-film were scanned and their effective surface area was determined. A residual gas analysis (RGA) of the C-film on Cu sample was performed to estimate the hydrogen content in the prepared carbon film. The sample was kept in a MILA-3000 Image Furnace and heated up a temperature of 600 °C, at a steady rate of 9 °C min^{-1} and a SRS RGA300 was used to analyze the residual gases. The vapor pressures of N_2, O_2, H_2 and H_2O were observed over the period of the run.

To test the electrochemical performance, the carbon film was deposited for 360 min on a circular Cu foil of 1.59 cm diameter. The Cu foil was weighted before the deposition in high precision scale with a resolution of 0.01 mg in order to measure the weight of the carbon film after deposition. After deposition for 360 min, the

acquired carbon film was ~1.1 μm thick and weighed 0.39 mg. The electrochemical performance of the sputtered carbon film on Cu foil was studied by assembling two-electrode HS-Test Cell (Hohsen Corp., Japan) with lithium metal as reference/counter electrode in a 1 M LiPF6/EC:DEC (1:1 in volume) electrolyte (Ferro Corporation, USA). The working electrode was the sputter deposited carbon film. All manipulations were performed in a glove box (MBraun, UniLab, USA) filled with purified argon. The moisture content and oxygen level were less than 1 ppm inside the glove box. The assembled cells were discharged and charged galvanostatically at 0.2 C rate, between 3.0 and 0.005 V using a Potentiostat/Galvanostat (Autolab, PGSTAT30, EcoChemie, The Netherlands). The C-rate was calculated based on the theoretical capacity of graphite which is 372 mAh g^{-1}. For 0.2 C rate, a current of 74.4 mA g^{-1} was used to perform the charge–discharge.

3. Results and discussions

The SEM images of the top view and cross-section of the as-sputtered carbon on copper foil are shown in Fig. 1. The top view image in Fig. 1a reveals a smooth morphology of the deposited film which is very critical in terms of the electrochemical properties of the system. The cross-sectional image shown in Fig. 1b was typically utilized to estimate the thickness of the carbon film, which was found to be very uniform through the entire film, and was also confirmed by step profilometry. Based on the sputtered time which was 60 min, the rate of carbon deposition was calculated to be 3.3 nm min^{-1}. In addition, XRD scans revealed that carbon film was amorphous with no discernable diffractions peaks as expected (data not shown).
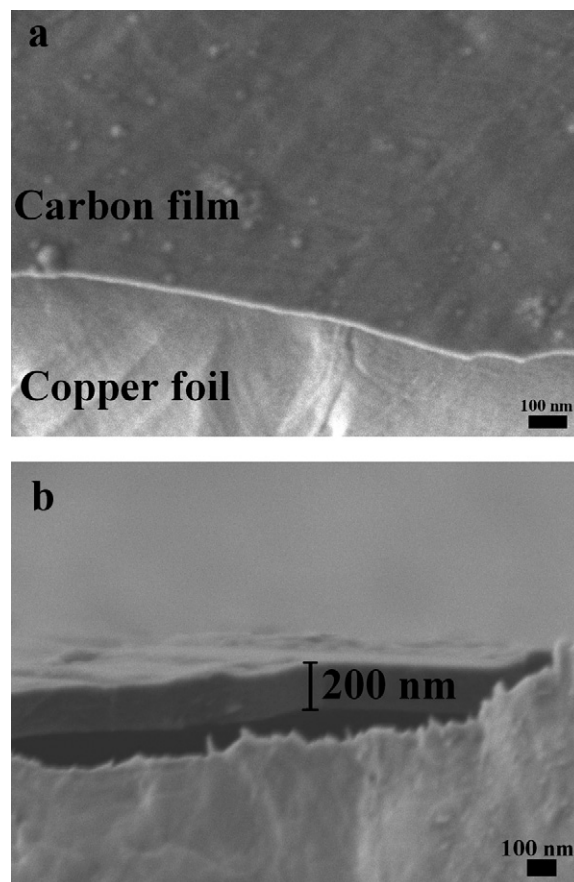

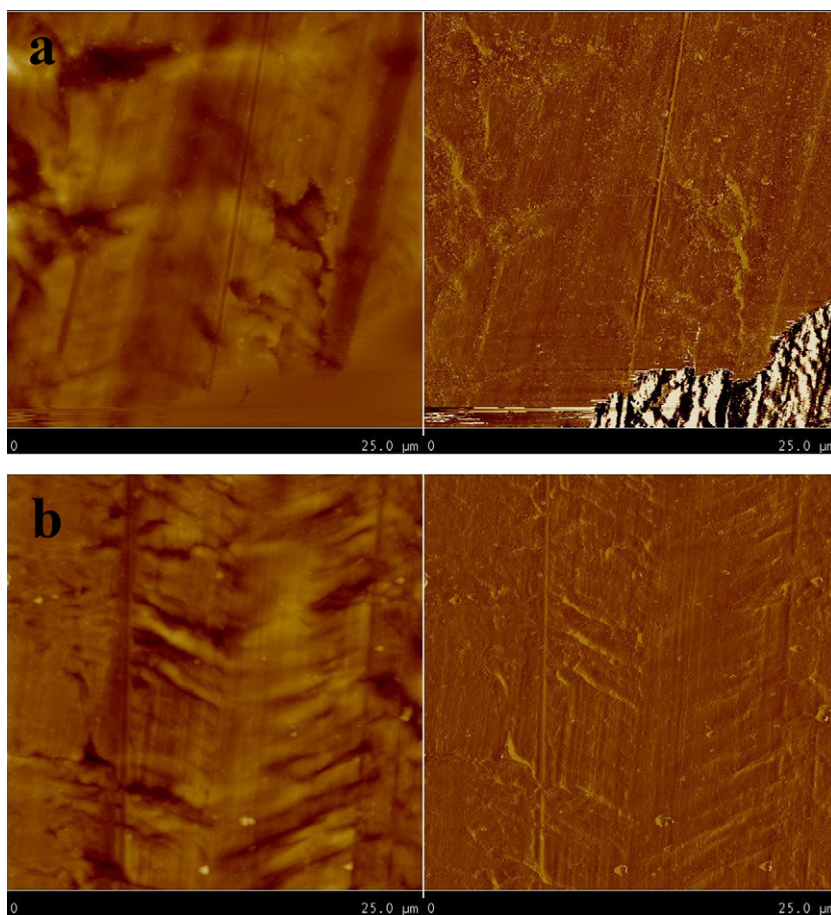Fig. 1. (a) Top view and (b) cross-sectional view SEM images of a carbon film on Cu foil.

Fig. 2. Typical AFM images of (a) bare Cu foil and (b) sputter deposited carbon film.

The representative AFM scans recorded for the Cu foil substrate and the C-film (360 min deposition) are shown in Fig. 2a and b, respectively. The increase in the effective area of sputter deposited C-film over the bare Cu foil was found to be less than 2%, indicating that deposition did not lead to any significant change in the surface area. Another important aspect of the deposited film in terms of electrochemical perspective is its roughness factor. The root mean surface (rms) roughness of the copper foil and the carbon film was ~44.4 and 25.6 nm, respectively as measured by AFM, which indicates that the films were rather smooth supporting the SEM measurements. The effective surface area in these AFM images was measured to be only 1.2% larger than the projected flat surface area.

The above results from SEM and AFM studies clearly indicate a new type of electrode with amorphous carbon exhibiting a very low surface area with no visible pores. This is an important finding as the conventional amorphous carbons generally exhibit a high surface area with a wide distribution of pores which greatly reflects on the electrochemical performance when used as a battery active material.

Since it is clearly evident from the above studies that the prepared carbon films do not have high surface area or porous structure, another factor to be considered for the irreversible capacity in the first cycle is the hydrogen content [6,7]. As described in Section 2, RGA studies were performed for N_2, O_2, H_2 and H_2O for a period of the run and the results are shown in Fig. 3. The pressure of desorbed hydrogen is significantly lower compared to the other molecules including H_2O. The origin of the hydrogen in the prepared carbon film is more likely from *ex-situ* exposure to the atmosphere or due to the dissociated water molecules. The influ-

ence of such an amorphous carbon film with a low surface area and low hydrogen content on the electrochemical properties in Li-ion batteries is studied for the first time and the details are discussed in the next section.

The galvanostatic charge–discharge curves for the carbon film are shown in Fig. 4. As can be seen from the figure, the topotactic process resembles that of a pure non-graphitic carbon without any staging mechanism. In the case of a graphitic carbon, the lithium insertion reaction occurs well below 0.5 V at three different stages until the formation of LiC_6 [10]. This formation reaction of one
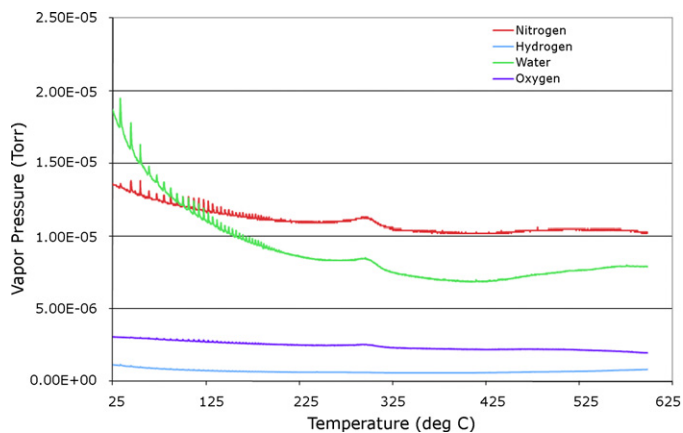

Fig. 3. Profiles of different gases studied using RGA for the prepared C-film on Cu foil. The samples were heated from 25 to 600 °C at heating rate of 9 °C min^{-1}.
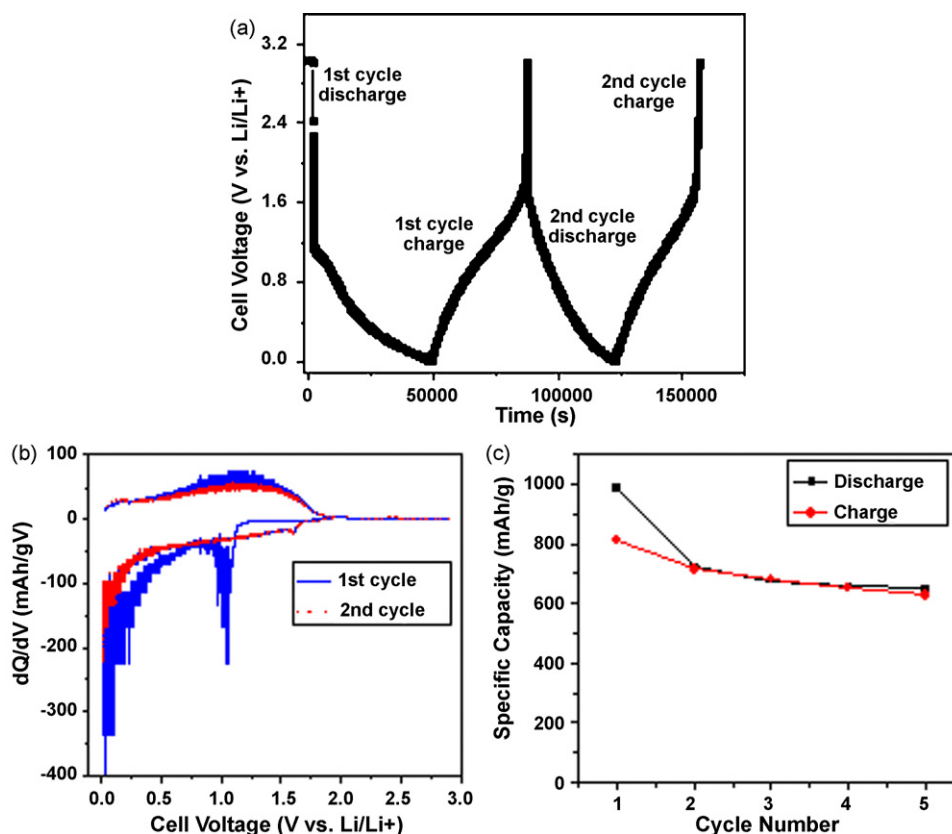
Fig. 4. (a) Charge–discharge curves for the sputter deposited carbon film at 0.2 C rate in a 1 M LiPF6/EC:DEC electrolyte cycled between 3 and 0.005 V. (b) Differential capacity plots. (c) Cycling performance of the sputter deposited carbon film at 0.2 C rate in a 1 M LiPF6/EC:DEC electrolyte cycled between 3 and 0.005 V.

lithium atom for every six carbon atoms corresponds to the theoretical lithium storage capacity value of 372 mAh g^{-1}. However, in the case of disordered or amorphous carbon, the lithium insertion has no such stipulated staging process; instead it occurs over a range of voltages after the surface film formation reaction is completed. In order to further confirm the non-existence of any staging mechanism, the galvanostatic charge–discharge curves were differentiated with respect to the cell voltage and the plots are shown for the first two cycles in Fig. 4b. As expected, there is only one peak during the first cycle insertion of lithium which is the irreversible surface film formation reaction. This is mainly due to the surface film formation over the carbon film electrode because of the reaction with the electrolyte, which occurs at ~0.8 V. This film which is called as the solid electrolyte interface is ionically conducting and prevents further reaction of the electrode surface with the electrolyte once its thickness is large enough to prevent electron tunneling [10]. This reaction is limited only to the first cycle lithium insertion and it is irreversible as shown in the differential plot in Fig. 4b. In the second cycle there is no such peak at ~0.8 V. The most interesting factor here is the specific capacity value for the insertion and deinsertion reactions during the first and subsequent cycles. The first cycle Li insertion capacity was 987 mAh g^{-1} and the corresponding deinsertion capacity was 812 mAh g^{-1}, with an overall coloumbic efficiency of 82% which is extremely high for an amorphous carbon electrode. For the second cycle the efficiency improved further to 99% with a reversible capacity of 715 mAh g^{-1}. As shown in Fig. 4c, the insertion and deinsertion capacities were found to be 648 and 627 mAh g^{-1} after 5 cycles, respectively. The electrochemical performance observed for the amorphous carbon film is interestingly unusual and requires further attention.

In the case of graphitic carbon, the specific surface area will be only a few m^2 g^{-1}. This limits the surface film formation reac-

tion thereby accounting only for a minimal irreversible capacity in the first cycle. Moreover, the ordered structure of graphite allows the lithium ions to be intercalated in between the well-defined graphene sheets which are very favorable for lithium removal. In contrast, in the case of non-graphitic or amorphous carbon, the specific surface area will be in the order of 100–1000 m^2 g^{-1}, depending upon the precursor and the carbonization temperature [6–8]. Also, they exhibit a wide pore size distribution as well as a high hydrogen content depending upon the synthesis conditions [6–8]. All these factors prompt an extremely large first cycle irreversible reaction associated with the surface film formation reaction because of the decomposition of the electrolyte. The surface film formation and their physical and spectroscopic characterizations have been widely studied for both graphitic and non-graphitic carbon [11–13]. Generally, the disordered carbons were prepared from natural precursors such as sugar or rice husk [14,15], etc., or from polymer precursors such as poly (acrylo nitrile) [PAN], etc. [16], and in either case, there was a possibility of coexistence of hydrogen in the formed compound depending upon the temperature of preparation. The amount of hydrogen present in the synthesized carbon mainly depends on the nature of the precursor and the carbonization temperature, i.e., carbon materials prepared at higher temperatures (>1000 °C) are generally believed to have a lower hydrogen content [7]. In the case of carbon materials prepared by the pyrolysis of rice husk, there has been more than 67% irreversibility because of its huge specific surface area, ~1597 m^2 g^{-1} [14]. In other words, larger the specific surface area of the carbon, higher will be the irreversible and reversible capacities. Another important aspect of the pyrolytic carbon is their hydrogen content, which is dictated by the carbonization temperature. According to the earlier studies pertaining to disordered or low temperature carbon materials—when the hydrogen content of the

prepared carbon materials is higher, then the carbon material show a high first cycle irreversible capacity [6–9]. In general, the presence of a larger amount of hydrogen will always affect the reversible lithium capacity in any carbon material [7,15]. The reasons for such a behavior are beyond the scope of this manuscript and can be found abundantly in open literature [6,16].

In the present case, we have two major advantages despite the electrode material being amorphous; (1) very low surface area akin to graphitic carbon and (2) almost negligible hydrogen content in the film because of the high vacuum conditions during sputter deposition, which has been confirmed by the RGA studies discussed above. Also, from the SEM and AFM studies it was clearly evident that the carbon films are not porous and exhibit a very smooth morphology. Because of this surface morphology of the films we can estimate that the surface area of the electrode is almost similar to the geometrical area of the electrode. The calculated surface area for the deposited carbon film was $\sim 1.93\,m^2\,g^{-1}$. The above two advantages are well reflected in the electrochemical properties with a very high reversible specific capacity, at least twice that of graphitic carbon ($372\,mAh\,g^{-1}$) combined with a very low first cycle irreversible capacity.

Although the lower hydrogen content and the lower specific surface area relates more to the first cycle irreversible capacity, it is important to understand the reasons behind the larger specific capacity than that of a graphitic electrolyte. There are two possible reasons for such a behavior, (1) the thickness of the carbon film and (2) the structure of the amorphous carbon film and its porosity. The actual thickness of the sputter deposited carbon film is close to $\sim 1.1\,\mu m$ which is at least 100 times smaller than the conventionally coated disordered or graphitic carbon electrodes. This is very critical when considered for the electrochemical performance, where the participation of the electrode is important. Here, as electrode thickness is much smaller, the active participation of the entire material is possible at all current rates which results in a completely reversible electrochemical storage of lithium. This greatly improves the effective capacity of the material, which is deprived in most of the conventionally coated electrodes.

Another important aspect of the sputter deposited carbon material is its density and the disordered structure of the carbon film. Since the sputtering process was carried out under low pressures, the film is expected to be dense and the presence of carbon materials with high porosity is very limited. The pores may be favorable for the insertion of Li ions but may not be favorable for their removal. This further increases the first cycle irreversible capacity beyond that originated from the large surface area. The absence of high porosity in the present case will lower the irreversible capacity. In the case of the graphitic carbon, the structure is well-aligned graphene sheets with limited available space for the storage of lithium ions between the individual graphene sheets. However, in the present case, since the carbon is amorphous, the structure is not well defined as in the parallel plates of graphene. Instead, it is randomly oriented leading to more available lithium storage space as seen, akin to the disordered carbon prepared from organic or natural precursors.

There are a few earlier studies involving carbon films coatings for lithium battery studies [9,17,18]. The sputter deposited amorphous carbon films seem to be much better in performance and it offers a simple fabrication technique when compared with the earlier reports available for carbon films. In the case of RF magnetron sputtered carbon film on ITO substrate with amorphous carbon as target, there has been a huge first cycle irreversible capacity [Ref. [6], Fig. 1 (inset)]. Although, the authors have not quantified the specific capacity in terms of weight, as can be seen from the time for insertion and deinsertion reactions there has been at least a 70% irreversible capacity in the first cycle [9]. In the case of carbon films prepared by the pyrolysis of wood, there has been a high tempera-

ture for the synthesis of the films ($1100\,^\circ C$) where the films exhibit both low reversible and irreversible capacities $\sim 300\,mAh\,g^{-1}$ [17]. In the case of plasma CVD derived carbon films, there has been a huge first cycle irreversible capacity which may be due to the use of acetylene as the source for the carbon and the preparation conditions [18].

Furthermore, in conventional coating techniques, additional components such as a polymeric binder for better adhesion of the active material to the current collector are necessary and should be added, which is not present in this case. The binder is generally an electrochemically inactive material but amounts for the increase in the electrode weight. Hence, the present sputter deposition technique is very advantageous both in terms of effective usage of the material and the electrochemical performance with improved energy density.

Considering and weighing all the factors for both the graphitic and non-graphitic carbons, the present sputter deposited carbon exhibits the advantages of both. Main reasons for such an improved behavior of the sputter deposited carbon film over its other counterparts are its low surface area and roughness, low thickness, low porosity, and negligible hydrogen content.

From this preliminary study, the main disadvantage seems to be the capacity fading. After 5 cycles at 0.2 C, the columbic efficiency is 77%. This may be due to the weak adhesion of carbon film to the copper current collector. Further work is in progress to improve the adhesion of the sputter deposited carbon on Cu foil with a specific focus on the effect of thickness of the film and rate capability of such a carbon film.

4. Conclusions

In summary, amorphous carbon films have been successfully prepared directly on copper current collectors. The prepared films were smooth and uniform with a root mean square roughness of about 26 nm as evidenced by AFM and SEM studies. XRD scans revealed that carbon films were amorphous. The electrochemical performance of the sputtered carbon film is very promising with a reversible capacity of $812\,mAh\,g^{-1}$ for the 1st cycle with an efficiency of 82%. This is remarkably high and is mainly because of the low surface area, low film thickness, negligible hydrogen content and low porosity and has not been reported earlier for any amorphous carbon material. Hence, it can be concluded that this sputter deposition technique offers a unique combination of low temperature, low porosity and low surface area carbon material with negligible hydrogen content, which is very much sought in the present day battery community. Improving the adhesion may result in further improvement in the electrochemical performance, which will be an ideal binder-free negative electrode material for the future Li-ion batteries. Further work to extend this method to prepare other transition metal oxides is in progress which will be very interesting both in terms of energy and power densities of the battery.

Acknowledgements

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