

Carbon film covering originated from fullerene C₆₀ on the surface of lithium metal anode for lithium secondary batteries

Arenst Andreas Arie · Oleg M. Vovk · Jin O. Song ·
Byung Won Cho · Joong Kee Lee

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Abstract Carbon films from fullerene C₆₀ were coated on the surface of lithium metal for the anode of lithium secondary battery. In order to investigate the relationship between the electrochemical characteristics of the carbon films and deposition technique, three different vacuum techniques were employed such as RF (radio frequency)—magnetron sputtering of C₆₀, plasma assisted thermal evaporation of C₆₀ and ion beam assisted thermal evaporation of fullerene C₆₀. From the physical and chemical characterization tests, we found that the carbon films produced by those above techniques mainly consist of sp²/sp³ hybridized amorphous carbons. Electrochemical tests implied that the cyclic performance was enhanced by the fullerene C₆₀ coating on lithium metal anode in comparison to the pure lithium metal one. This enhanced performance is due to the formation of thin carbon film on the surface of lithium metal anode which plays a role as a passive layer against the side reaction between lithium metal and the electrolyte.

Keywords Fullerene C₆₀ · Vacuum deposition techniques · Carbon films · Anode

A. A. Arie · J. O. Song · B. W. Cho · J. K. Lee (✉)
Advanced Energy Materials Processing Laboratory,
Battery Research Center,
Korea Institute of Science and Technology,
P.O. BOX 131, Cheongryang, Seoul 130-650, Korea
e-mail: leejk@kist.re.kr

A. A. Arie
e-mail: arenst@yahoo.com

O. M. Vovk
Department of Crystalline Materials of Complex Compounds,
Institute for Single Crystals,
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

1 Introduction

In the past decades, a lot of research has been focused to find new anode materials to substitute graphite to improve the specific energy capacity for lithium secondary batteries such as silicon thin film [1–3], carbon–metal composites [4–5] or composites between silicon and metals have been explored as new anode materials [6]. As a pure metal, lithium is a promising anode material for applications since it has a relatively high anode potential (−3.045 volt vs standard hydrogen electrode) and a high specific capacity (3,860 mAh/g). Next to the advantages of the lithium properties, it has a limitation in practical use. Prolonged dissolution and deposition cycling cause dendrite formation of the lithium metal, which give serious problems in safety and performances of lithium battery [7]. The dendrite is simply a passive layer which caused by the contact between lithium metal anodes and the liquid electrolyte. Therefore we used carbon material to coat the lithium metal so the lithium ion could have reversible intercalation/de-intercalation reactions with the carbon, to form a lithiated carbon. This kind of reactions prevents the dendrite formation and finally improves the performance of the battery [8].

The main source of carbon material being used as a precursor in the experiment is fullerene C₆₀ [9]. The fullerenes, discovered in 1985, are a family of carbon allotropes and they are similar in structure with graphite. Fullerenes are cage-like all-carbon molecules which can form polymeric materials if they are excited to high intensity photon, electron irradiation or plasma operation. A wide variety of chemically modified fullerenes have been synthesized and one of the applications is in the area of electrochemistry [10–11].

In this work, we used fullerene coating on the surface of lithium metal anode for lithium secondary battery by employing three kinds of vacuum coating techniques. It

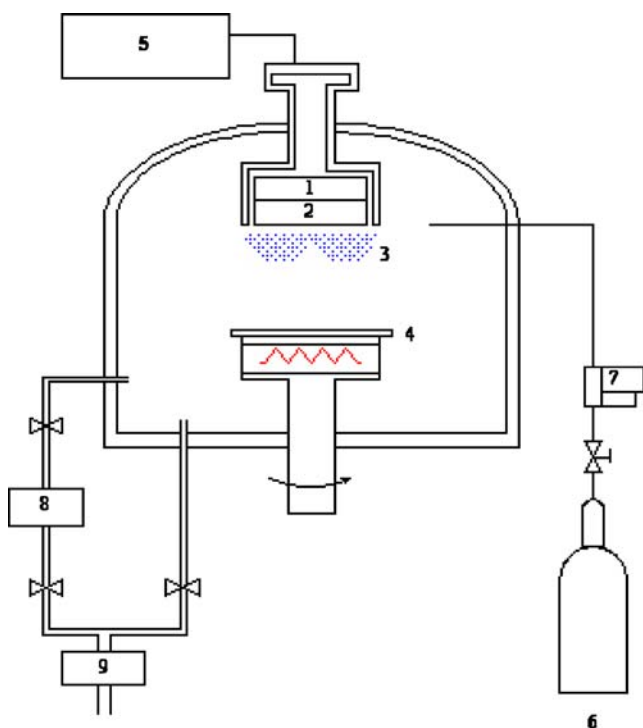


Fig. 1 Schematic diagram of the RF magnetron sputtering technique for fullerene C₆₀ coatings on the surface of lithium foil: 1 graphite target, 2 C₆₀ on graphite target, 3 closed plasma, 4 substrate(lithium metal), 5 RF-generator, 6 argon gas, 7 MFC, 8 turbo pump, 9 rotary pump

was expected that the fullerene layer acted as a passive layer to control the dendrite formation and as the result, an enhanced electrochemical performances of lithium metal anode can be achieved.

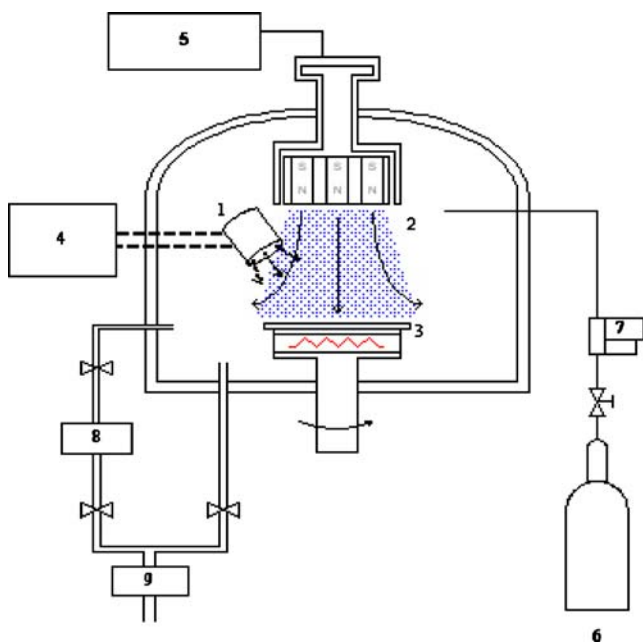


Fig. 2 Schematic diagram of the plasma assisted evaporation technique for fullerene C₆₀ coatings on the surface of lithium foil: 1 Knudsen cell, 2 open plasma, 3 substrate (lithium metal), 4 temperature control box, 5. RF-generator, 6 argon gas, 7 MFC, 8 turbo pump, 9 rotary pump

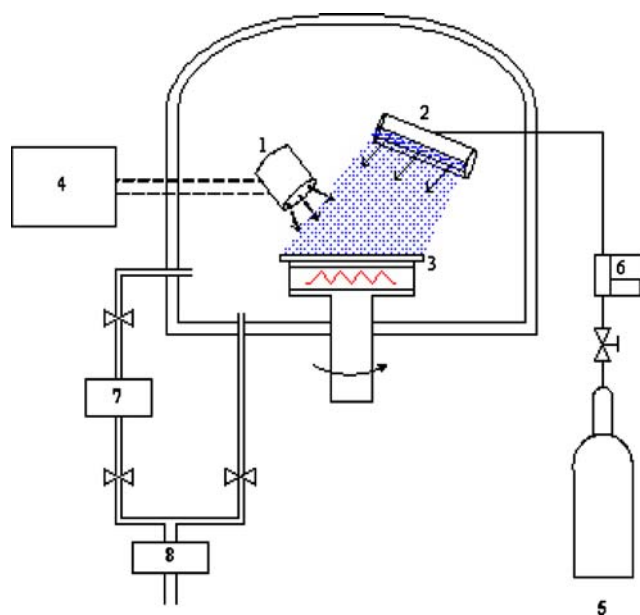


Fig. 3 Schematic diagram of the ion beam assisted evaporation technique for fullerene C₆₀ coatings on the surface of lithium foil: 1 Knudsen cell, 2 ion beam source, 3 substrate (lithium metal), 4 temperature control box, 5 RF generator, 6 argon gas, 7 MFC, 8 turbo pump

2 Experimental

Three different vacuum techniques were applied to deposit carbon film, using fullerene C₆₀ on the surface of lithium metal. Those are the radio frequency (RF) magnetron sputtering, plasma and ion assisted thermal evaporation of C₆₀, which are shown schematically in Figs. 1, 2 and 3, respectively. For all of them, the base and working pressure were maintained at 2.10⁻⁵ and 3.10⁻² torr, respectively. As a substrate material to be coated, lithium metal with thickness of 75 μm was prepared. Fullerene C₆₀ was used as a carbon precursor. There was a pretreatment for the lithium metal, before the coating process with the C₆₀ took place. It was done by applying a plasma operation to

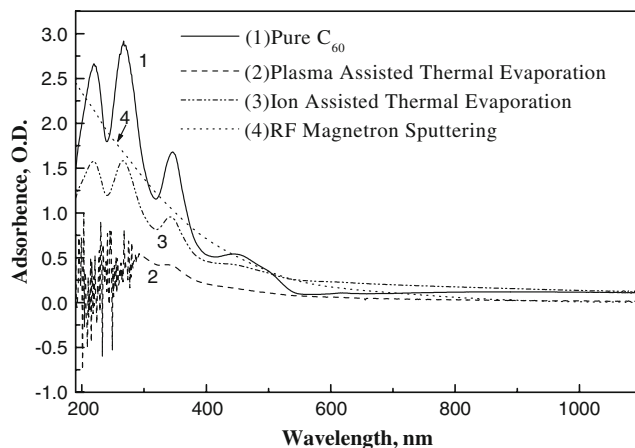


Fig. 4 UV-Vis spectra of the pure C₆₀ film and C₆₀ coated films obtained by three vacuum techniques

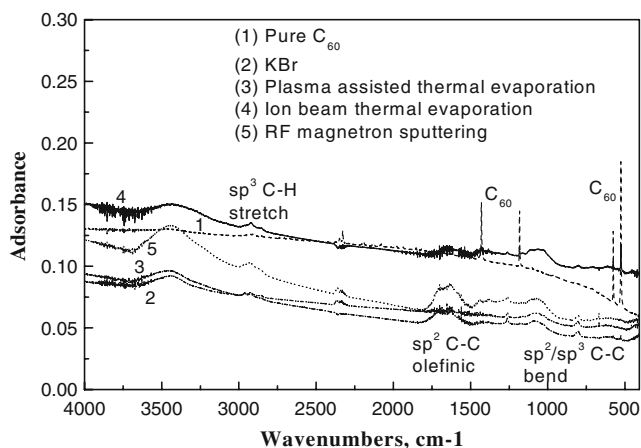


Fig. 5 FT-IR spectra of pure C_{60} film and C_{60} coated films obtained by three vacuum techniques

remove an oxidized layer on the lithium surface. This pretreatment process was conducted at plasma power of 50 W and 30 min of operation time.

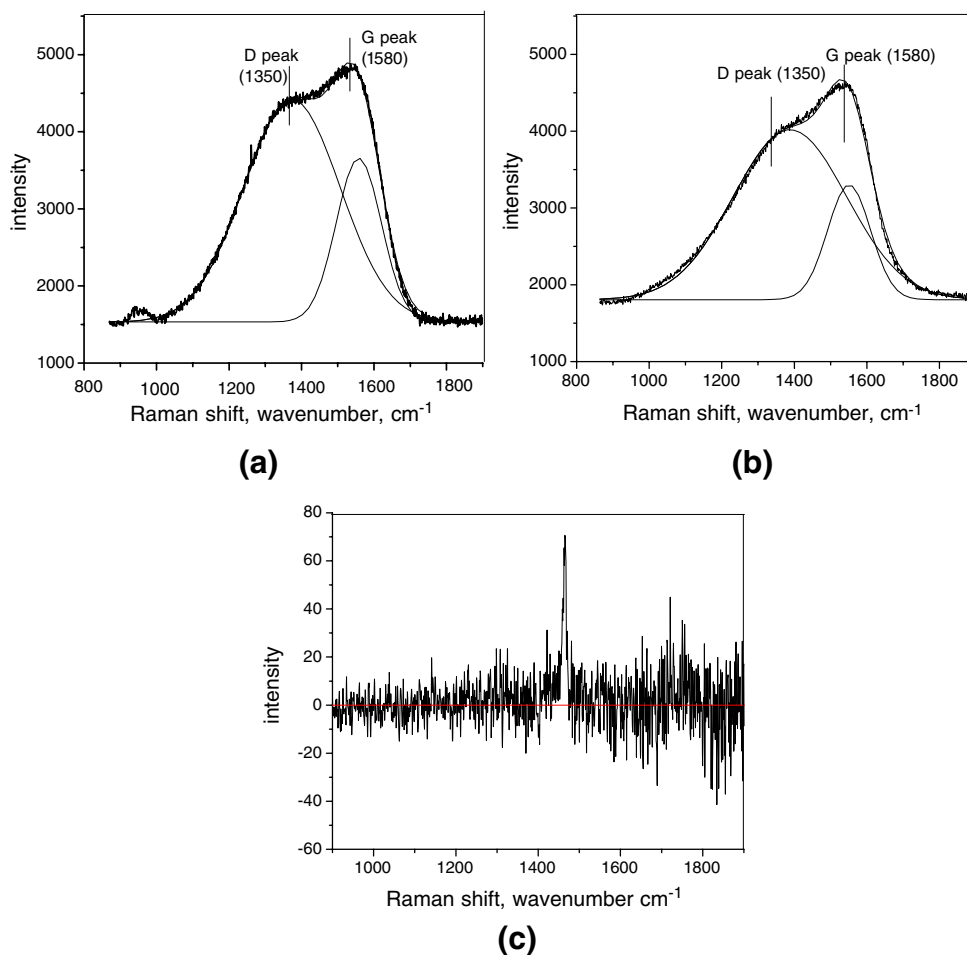
The first technique applied was the RF magnetron sputtering technique. Initially, the C_{60} film was prepared as a sputter target. It was done by thermal evaporation of C_{60} powder (99.5%, Astrin Inc, Russia) onto a graphite disk

with a diameter of 74 mm. This process was operated at radio frequency power of 130 W; argon flow rate of 30 sccm and evaporation time of 5 h. After the preparation of C_{60} on graphite target, we could proceed with the RF sputtering by using lithium metal as a substrate to be coated.

The second technique was the plasma assisted thermal evaporation of C_{60} . The C_{60} powder was put at the Knudsen cell in which it was heated up at 550°C and then was evaporated. As depicted in Fig. 2, this system was an open plasma process where the direct interaction among the plasma, argon gas and evaporated C_{60} took place. The operation was set at radio frequency power of 100 W; argon flow rate of 30 sccm and deposition time of 30 min.

The third technique to coat the lithium foil was the ion beam assisted thermal evaporation of C_{60} . In this technique, the C_{60} powder was also placed in the knudsen cell as when it was evaporated at 550°C . The lithium metal as a substrate was exposed to an ion beam source (Kaufman type) which was connected to DC power source of 220 V. This ion beam source ionizes and dissociates the flowing argon gas. The argon flow rate and deposition time were the same as those of previous techniques.

Fig. 6 Raman spectroscopy of C_{60} films obtained by RF magnetron sputtering (a), Plasma assisted evaporation (b) and ion beam assisted evaporation (c)



In order to compare the electrochemical anode performance of the fullerenes C_{60} coated lithium, the electrodes of half cell for lithium secondary battery were manufactured. Half cells were employed instead of the full ones since the main aim here was to investigate the properties of the C_{60} coated lithium metal electrode as an anode of lithium ion battery. We expect that C_{60} layer acts as a passive film during electrochemical performance. It may have an important role to control dendrite formation during repeated charge-discharge process.

The electrodes were cut into 2×2 cm pieces and dried in a vacuum and dry chamber. Lithium cobalt oxide (SKC, Korea) was used as a counter electrode and the separator was the polypropylene-based film. The electrolyte used in this test was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC; 1:1:1 in v/v). The fabricated half cell was galvanostatically charged and discharged at room temperature in the voltage range 3.0–4.3 V versus Li/Li^+ at rate range of 0,2 C and 0,5 C (Maccor SERIES 4000). Impedance experiments were executed at frequency range from 10^{-2} to 10^5 Hz (IM 6 Zahner).

The UV-Vis adsorption spectra of the obtained carbon films were recorded in the range 190–1,100 nm with resolution of 1 nm by HP Aglient 8453 UV-Vis spectrometer. The Raman spectra were recorded on Nicolet Almega XR dispersive Raman spectrometer (Thermo Electron

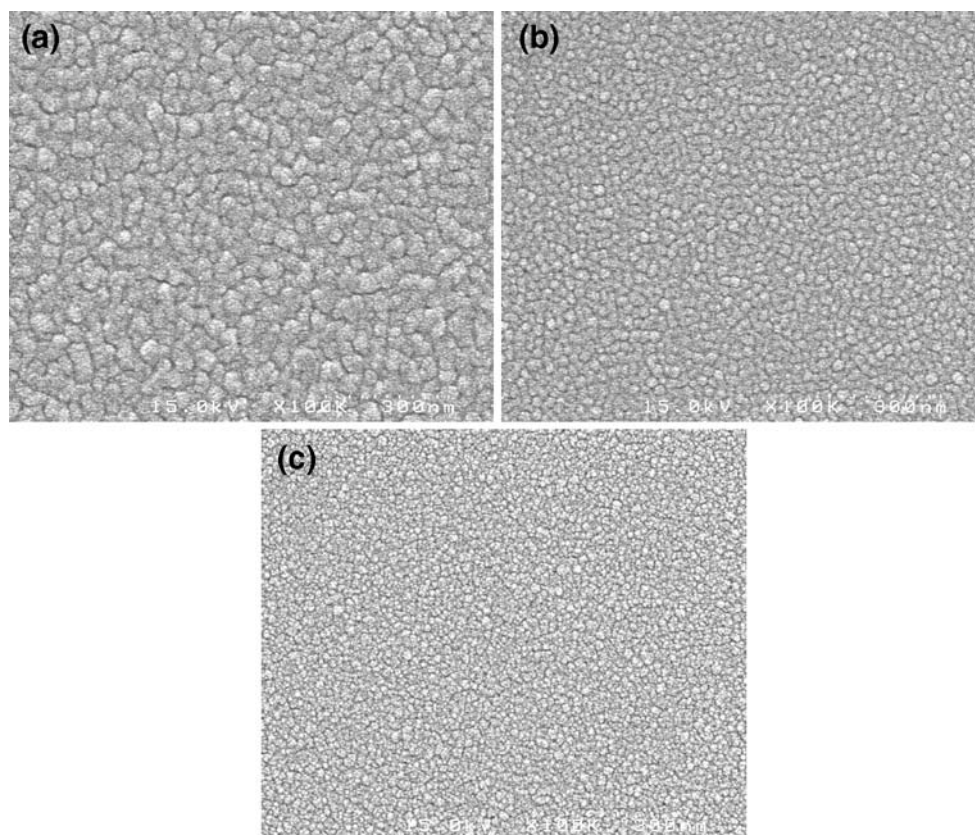
Corporation, USA) with the 633 nm line of He–Ne laser. The morphology of carbon films was examined using scanning electron microscope (SEM) analysis. The Infrared (IR) experiments were carried out in the range 500–4,000/ cm of wave number (Hitachi 400).

3 Results and discussion

3.1 The optical property of fullerene C_{60} films

The UV-Vis adsorption spectroscopy was used to characterize the optical property of the carbon films obtained by each vacuum evaporation technique of the C_{60} . Figure 4 shows the UV-Vis spectra of pure C_{60} and three carbon films obtained by the three different vacuum techniques (RF magnetron sputtering, plasma and ion assisted). It can be seen from Fig. 4 that the absorbance plot of the carbon film resulted from the ion beam assisted technique has a similarity with that in the case of pure C_{60} . Both of them showed three peaks in the range of 200 to 400 nm of wavelength. Especially for the spectra given by the ion beam case gives smaller peak spectra in comparison to the pure C_{60} spectra. It means that this carbon film could contain a portion of initial fullerene C_{60} . From Fig. 4, we can also see that the other two spectra obtained by the sputtering and plasma assisted, are smooth without any

Fig. 7 SEM images of fullerene C_{60} film deposited by three different techniques: Ion beam assisted evaporation (a), Plasma assisted evaporation (b) and RF sputtering (c)



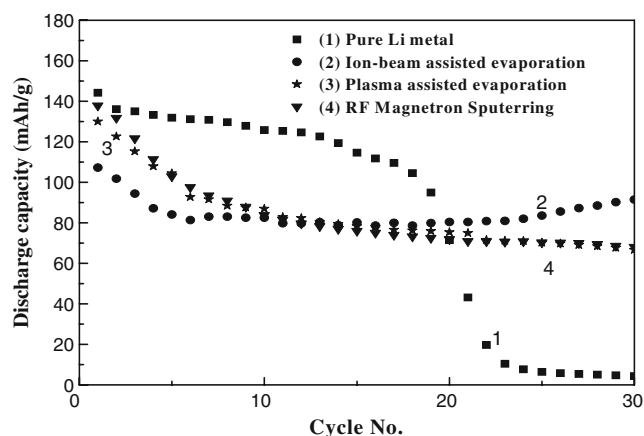


Fig. 8 The cyclic performance of pure lithium electrode and fullerene C_{60} coated lithium electrode obtained by three different techniques

features that characterize fullerene molecule. It could be explained that during the operation of sputtering and plasma assisted, the C_{60} cages were decomposed to other form of carbon molecules. The plasma and ion bombardment to the C_{60} target gave an effect to the decomposition of the C_{60} .

3.2 The bonding property of fullerene C_{60} films

The bonding states of C and H especially were characterized by using Fourier transforms infra red (FT-IR) measurements. Figure 5 shows the comparison of FT-IR absorption spectra among the various carbon films (pure one and those obtained by three applied techniques) in the range of 500–4,000 cm^{-1} . In this range for all carbon films produced by three techniques, we can find different types of crystalline structures of the carbon films. The absorption peak of the carbon films at 2830 cm^{-1} is related to the main content of hydrogen in form of sp^3 stretching mode [12]. The peak at 1,700 cm^{-1} is caused by sp^2 olefinic C–C vibration mode. The wave numbers at 1,220–1,300 cm^{-1} is attributed to C–C bending modes of sp^2 and sp^3 carbon. Moreover we can see that the spectra of pure C_{60} have four peaks at 500, 520, 1,200 and 1,450 cm^{-1} but for other spectra of carbon films we can find that there are many small peaks in the vicinity of those four peaks. Interpreting this fact, we could say that during the deposition process of carbon films using three applied technique, the C_{60} molecules were dissociated due to the collision and reaction with the argon plasma and then finally deposited on the surface of lithium foil.

3.3 The structural property of fullerene C_{60} films

The Raman spectra of carbon films obtained by the technique of sputtering or plasma assisted and ion beam assisted evaporation of fullerene C_{60} , is depicted in Fig. 6.

The spectra of the films resulted from the technique of sputtering and plasma assisted split into two peaks, known as D (disorder) peak and G (graphite like) peak. The D peak and G peak are given at wave numbers of 1350 and 1580 cm^{-1} as shown in Fig. 6(a) and (b). The G peak occurs at all sp^2 sites such as olefin chains and aromatic rings and D peak is related to the presence of aromatic rings. G peak is a good indicator of disorder carbon and shows dispersion only in amorphous network [13]. Therefore we could say that the initial C_{60} cages were decomposed became other structure of amorphous carbon. Fig. 6(c) shows that the spectra of fullerene film, comes from the ion beam technique, has a broad band which indicates no disorder structure of carbon formed during the ion beam operation.

3.4 Surface morphological property of fullerene C_{60} films

Scanning electron microscopy (SEM) was applied to have the characteristic of surface morphologies of the carbon films obtained by the three different vacuum techniques. Figure 7(a) shows the surface morphology of carbon film deposited on lithium metal resulted from the technique of ion beam assisted. Figure 7(b) gives the surface morphology of carbon film resulted from the technique of plasma assisted and finally the surface morphology of carbon film resulted from the RF sputtering is depicted in Fig. 7(c). From these images, we can see that the thin carbon films were coated on most of the surfaces of lithium metal. Furthermore, we can observe that the finest particles in size are given by the carbon film obtained by the technique of sputtering. On the contrary the carbon film obtained by the technique of ion beam gives the coarsest particles in size. These facts are due to the uncompleted decomposition of C_{60} cages during the operation of ion beam assisted. Its surface still contains the C_{60} molecules as well as the decomposed C_{60} .

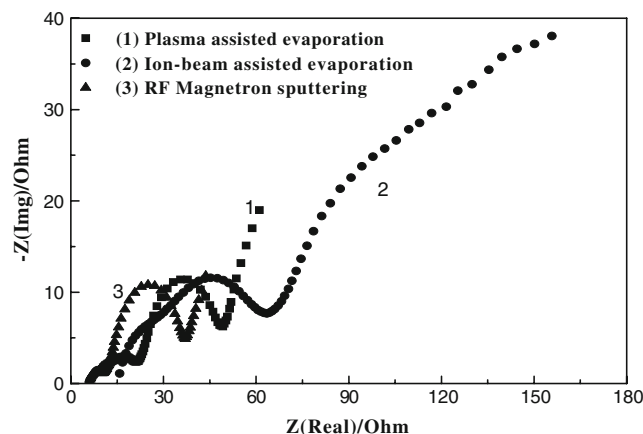


Fig. 9 Nyquist plots of fullerene C_{60} coated lithium electrodes obtained by three different techniques

3.5 Electrochemical property of fullerene C₆₀ coated lithium electrode

Figure 8 shows the discharge capacity with respect to the repeated cycle, each of them for the half electrochemical cell. This cell was fabricated from the pure lithium metal and the three carbon coated lithium metal electrode, obtained by three different techniques: RF-magnetron sputtering, plasma and ion assisted deposition. It can be observed from Fig. 8 that the pure lithium cell is fading after the 20th cycle due to extraction and dissolution of lithium electrode, forming dendrite deposition on the surface of the electrode. For the fullerene C₆₀ coated lithium electrodes obtained by all techniques, they showed an improvement by means of cyclic performance compared to the pure lithium cell. Until the 30th cycle, they showed more stable cyclic performance. This fact can be explained that the presence of carbon coatings on the surface of lithium metal act as a passive layer against the side reaction between the electrode and electrolyte. In other words, the carbon films act to protect the lithium electrode against the dissolution of lithium and maintain their mechanical structure during the repeated cycles. The same phenomena were given by DLC films coated on the surface of lithium anode [14]. Moreover it was found that by comparing the cyclic performance of the electrode produced by those above techniques, we can see that until the 30th cycle, there are no significant differences among them. *Special remark should be informed about the cyclic test*; it was conducted for 30 cycles on each lithium electrode. Because of the nature of half cells, as explained in the experimental section, it was not possible to continue the test until hundred of cycles. However, we showed that C₆₀ coated lithium metal electrode play an important role to control dendrite formation during electrochemical cycling.

The second test being used in this work to examine the electrochemical property of the electrode is the impedance spectroscopy. From the Nyquist plots of fullerene C₆₀ coated lithium electrode, which is depicted at Fig. 9, we can notice that the shortest diameter of semi-circle is shown by the electrode obtained by RF sputtering technique. Since the diameter of semi circle is equivalent with the interfacial impedance, it means that the RF sputtering gives the smallest interfacial impedance among those above techniques. Impedance tests also reveal that the SEI (Solid Electrolyte Interphase) is formed by interfacial reaction between the electrode and electrolyte.

4 Conclusions

Three different technique of vacuum system have been employed in this experiment to deposit carbon films, comes from fullerene C₆₀, on the surface of lithium metal electrode. The fullerene C₆₀ coated lithium metal from three kinds of techniques used as an anode of lithium ion secondary cells and we found that the surface coatings of C₆₀ enhanced the cyclic performance of the lithium anode. The smallest interfacial impedance was given by the fabricated electrode obtained by the sputtering technique. From the characterization of thin carbon films, using UV/VIS, FTIR, SEM and Raman test, we observed that the sputtering and plasma assisted technique completely decomposed the initial fullerene C₆₀ molecules. The carbon films play an important role to act as a passive layer during repeated charge and discharges cycles. The identified carbon structures in the thin films mostly consist of sp²/sp³ hybridized amorphous carbons. Future research has to be focused on the optimization of each technique applied in this work, especially for the RF magnetron sputtering. The plasma power can be varied to have an optimum cyclic performance and better morphology.

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