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IN SITU RAMAN SPECTROSCOPY OF LITHIUM ELECTRODE SURFACE IN AMBIENT TEMPERATURE LITHIUM SECONDARY BATTERY

Final Report

September 1992

by

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This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4554310 with the Lawrence Berkeley Laboratory.

Abstract

Raman spectroscopy was used to characterize surface layers on lithium electrodes in different solvents such as propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and polyethylene glycol 400 dimethyl ether (PEG400DME). Both DMC and DEC were used singly, and also mixed with either methyl acetate (MA) or methyl formate (MF). The Raman spectra showed that passive films formed on the Li surface in different solvents may have different chemical structures, which changed during the charging and discharging processes.

Raman spectroscopy was also applied to characterize zinc electrode surfaces in alkaline solutions. The results suggested that ZnO and $Zn(OH)_2$ formed on the Zn electrode when a passive potential was applied.

A solid film of fullerene C_{60}, which could be used as a cathode in Li rechargeable batteries, was examined in the PEG400DME solution by both electrochemical and Raman spectroscopy. Cyclic voltammograms (CVs) showed five redox peaks which suggested the formation of C_{60}^{-}, C_{60}^{2-}, C_{60}^{3-}, C_{60}^{4-}, and C_{60}^{5-}. Raman spectra obtained from a thin C_{60} film indicated that the thin fulleride film dissolved in the PEG400DME/$LiClO_4$ solution at negative potentials.

Brief Description of Project

The main objective of this project is to characterize the surface layers on lithium electrodes in nonaqueous solvent-electrolyte systems by Raman spectroscopy. The formation of passive layers on cathodically deposited lithium is considered to have a strong influence on the rechargeability of lithium secondary batteries. The characterization of the passive layers on the lithium surface should provide information to improve the performance of lithium secondary batteries. Raman spectroscopy was also used to characterize the surface of other electrodes such as Zn and C_{60} films.

Experimental Section

The electrochemical cell and details of the experimental set-up for in-situ Raman spectroscopy were described in previous final reports (3/15/1986-6/30/87 and 7/1/87-7/31/88). The purification procedures for PC and supporting electrolytes ($LiAsF_6$ and $LiClO_4$) were also described in these reports. DMC, DEC, MA, and MF were dried in activated Linde 4A molecular sieves for 48 hours, then they were further purified by vacuum fractional distillation under an Ar atmosphere. Polyethylene glycol 400 dimethyl ether (PEG400DME) received from Fluka Chemical Corp. was dried by lithium ribbon (Fluka) for 4 days before use. The fullerene C_{60} received from Texas Fullerene Company (99.9% purity) was used as received. The electrochemical experiments for C_{60} were carried out in a VAC model dry box with high purity Ar (oxygen level was less than 0.5 ppm). The C_{60} film electrodes were prepared by coating 5-30 μl of 1 mM C_{60} in CH_2Cl_2 solution on the GC electrode surface (either 3.0 mm or 33 μm dia) and then evaporating the solvent.

Results and Discussion

Li electrode in DMC, DEC, and mixed solvents with MA and MF. Raman spectroscopy was carried out at a silver electrode surface after depositing thin lithium films (50, 150, 250, 350, 500, and 1000 Å) in dimethyl carbonate (DMC) solution with 1.0 M $LiClO_4$. A conventional two-compartment cell was used, and the solution was transferred from the cell compartment to the reservoir before recording the Raman spectra. An Ar^+ laser was used as the excitation source. Strong Raman signals appeared after 50 Å lithium film was deposited on silver by reduction of Li^+ in the solution. The intensity of Raman bands decreased sharply after 100 Å lithium film was deposited. The potential of the working electrode shifted from positive (0.2 V) at the start of deposition to negative (-0.48 V) after depositing 50 Å of Li. Several Raman bands from DMC and $LiClO_4$ were observed in the spectra recorded after deposition of 50-1000 Å Li films. Several bands (154, 348, 449, and 610 cm^{-1}) unrelated to the solution species were observed in the low frequency region after deposition of 50 Å Li (see Figure 1). These bands disappeared when thicker lithium films (100 and 500 Å) were deposited. Several broad high intensity bands (1502, 1559, and 1583 cm^{-1}) appeared after deposition of 350 Å lithium (see Figure 2). Basically, the same spectrum was observed after depositing 500 and 1000 Å lithium films. The potential of the working electrode shifted from 0.6 V to -0.3 V during deposition of the 150 Å Li film. However, the potential of the working electrode remained positive when thicker lithium films (250-1000 Å) were deposited. The Raman results and the potential changes observed during lithium deposition suggested that the lithium film is stable in DMC/$LiClO_4$ solution. The strong Raman scatterings, which were observed after deposition of 50 Å Li, may be due to the surface-enhanced Raman signal. The negative potential (-0.48 V) observed just after

deposition of the 50 Å film also indicated that the Li film remained briefly on the silver electrode surface. The low Raman intensity and the positive electrode potential after deposition of thicker films suggested that the lithium film reacted with the solvent and formed a reaction product. It is likely that the reaction product on the surface of the silver electrode reacted with lithium which was on the surface of the silver electrode. The broad Raman bands in the high frequency range (1502, 1559, and 1583 cm^{-1}) (see Figure 2) may be due to the reaction product of Li and DMC. On the other hand, several low frequency bands observed after deposition of 50 Å Li could be due to a passivating film on the lithium surface.

Contrary to the results obtained in the DMC solution, no significant Raman bands were observed at the smooth Ag electrode after depositing Li in DEC solution. The surface of the Ag electrode looked unchanged after deposition of a 500 Å Li film. The absence of Raman scatterings at the silver surface in the DEC solution may be due to the immediate reaction between Li and DEC. The color of the clear $LiClO_4$/DEC solution changed to brown after deposition of the Li films, and the brown color intensified as thicker Li films were deposited. No significant Raman bands were observed on the surface of the anodized silver after deposition of Li films (50-2000 Å). However, a broad strong luminescence band appeared in the 1200-1700 cm^{-1} range after Li deposition. The result suggested that the cathodically deposited Li film reacted with DEC to form decomposition products which are responsible for the observed strong luminescence.

The stability of lithium in DEC solution was also studied in the presence of methyl formate (MF) by using Raman spectroscopy. The ratio of DEC and MF was 1 to 1, and 1 M $LiClO_4$ was used as a supporting electrolyte. Raman spectra were recorded at a smooth

silver electrode (3000 Å thick) after depositing Li films (50, 100, 200, 350, 500, 1000, and 2000 Å) by constant current electrolysis. Raman spectra (100-1700 cm^{-1} range), which were recorded after deposition of Li films, did not show any significant bands. The surface of the silver electrode looked shiny during deposition of lithium films. The results suggested that the deposited Li thin film reacted with the solvent and then the reaction product immediately dissolved in the solution. White particles were formed in the solution during the Raman experiment. The results indicated that the lithium surface was more stable in mixed solvent of DEC and MF than in DEC. The white substance, which was formed during Li deposition, seemed to protect the Li surface. However, we could not characterize the white substance due to the lack of any significant Raman and fluorescence bands in the 100-1700 cm^{-1} spectrum range.

Li electrode in polyelectrolytes. The Cyclic voltammetric behavior of lithium electrodes in polyethylene glycol 400 dimethyl ether (PEG400DME) with $LiClO_4$ (0.6 M) was investigated in air-tight electrochemical cell filled with high purity argon gas. Thin-film silver (3000 Å thick) on a 1" x 1" x 1/16" glass plate was used as a working electrode, and lithium ribbon was used as both reference and auxiliary electrodes. A high cathodic current for the reduction of Li^+ to Li started at ~0 V when the potential was scanned from positive to negative. There was another low cathodic current which showed a peak near +0.6 V. An anodic peak current was observed at +0.9 V, and an anodic current with a shoulder at +0.5 V was also observed. It was observed that the lithium metal surface was stable in the PEG400DME.

Raman spectroscopy was carried out by using the same electrochemical cell. Either Ar^+ laser (514.5 nm line) or Kr^+ laser (647.1 nm line) was used as the excitation source.

When the Ar^+ laser was used as the excitation source, a strong broad luminescence appeared, and no significant Raman bands were observed. In-situ Raman spectra were recorded in the range between 150 cm^{-1} and 1700 cm^{-1}. The potentials applied to the silver electrode were between 3.0 V and -0.3 V. There were bands which were due to PEG400DME and ClO_4^- at all potentials (see Figure 3): 790, 804, 842, 1026, 1132, 1234, 1383, 1446, and 1471 cm^{-1} for the PEG400DME, and 929 cm^{-1} for ClO_4^-. Several bands including 247, 299, 346, 602, 635, 688, 719, 994, 1086, 1367, 1531, and 1613 cm^{-1} were observed at -0.1 V as shown in Figure 4 (only 500-900 cm^{-1} range is shown). These bands are unrelated to the solution species and were observed even when the potential was increased to 3.0 V. The results suggested that the above Raman bands may be due to a passive film which formed during lithium deposition on the silver electrode. The results also suggested that the passive film remained on the silver surface when the potential was reversed and moved to very positive potentials.

Li electrode in propylene carbonate. In-situ Raman spectroscopy of the lithium surface during the charging and discharging processes in propylene carbonated (PC) solution with $LiClO_4$ was carried out with a Kr^+ laser. The Raman spectra were recorded in the range between 150 and 1700 cm^{-1}. The formation of a passive film on the lithium surface could be seen during the charging process. The Raman spectra obtained in the PC solution with 1.0 M $LiClO_4$ at -1.0 V vs Li showed several Raman bands (1214, 1298, and 1549 cm^{-1} etc) which are unrelated to the solution species. Some of these Raman bands remained during the discharging process (potential was moved to 0.3 V and then to 1.0 V). When the charging and discharging processes were repeated several times, the Raman spectra gradually changed. A typical example is the observation of a 1240 cm^{-1} band during the first

charging process. The intensity of this band gradually decreased as the potential was changed to 0.3 and then to 1.0 V. A new band appeared at 1255 cm^{-1} during the potential cycle. The results suggested that the structure of the passive film may have changed during the repeated charging and discharging processes.

Zn electrode in alkaline solutions. Cyclic voltammetry and in-situ Raman spectroscopy studies of a Zn electrode (surface area (A) = 0.08 cm^2) were carried out in a 7 M KOH and 0.5 M ZnO solution. A zinc disk (A = 1.51 cm^2) was used as an auxiliary electrode. Cyclic voltammograms were recorded at a very slow scan rate (1 mV/s) and an equilibrium potential of -1.350 V (vs. Hg/HgO/7 M KOH reference electrode) was observed. When the potential was scanned in the positive direction, the Zn electrode started to dissolve and reached a constant current (212 mA/cm^2) at -1.1 V. The dissolution of the electrode suddenly stopped at -0.90 V (current dropped to nearly 0 amp). When the passive potential was reached, a constant current (25 mA/cm^2) was observed. The electrode potential was reversed at -0.7 V and scanned in the cathodic direction. When the potential reached to -1.04 V, the Zn electrode suddenly started to dissolve (current increased from 25 mA/cm^2 to 340 mA/cm^2). Cyclic voltammograms recorded at faster scan rates up to 20 mV/s were basically the same as those observed at 1 mV/s.

The above results are not consistent with those obtained by Goff et al.[1] The authors observed the equilibrium potential of -1.545 V vs. Hg/HgO 5 M KOH reference electrode, instead of -1.350 V which was observed in this experiment. The passive potential reported by the above authors (-1.26 V) was also different from ours (-0.90 V).

In-situ Raman spectra of the Zn electrode surface in 7 M KOH and 0.5 M ZnO solution were recorded at two potentials (-1.54 and -0.80 V). At the passive potential (-0.80

V), Raman bands were observed at 332, 390, 448, 480, and 564 cm^{-1}. The presence of both 332 and 449 cm^{-1} bands suggest the formation of ZnO at the Zn surface. The 390 cm^{-1} band indicates the presence of $Zn(OH)_2$ on the surface. The above spectrum was recorded after applying the anodic polarization potential (-0.80 V) for 2 hours. The dominant band observed at the equilibrium potential (-1.54 V) was the 480 cm^{-1} band which is probably due to $Zn(OH)_2$. These results suggest the possible formation of both ZnO and $Zn(OH)_2$ on the Zn electrode surface at the passive potential.

C_{60} film electrode in polyethylene glycol 400 dimethyl ether. A C_{60} thin film was prepared on a glassy carbon (GC) electrode surface. A linear sweep voltammogram showed five reduction peaks which suggested the formation of C_{60}^{-}, C_{60}^{2-}, C_{60}^{3-}, C_{60}^{4-}, and C_{60}^{5-} (see Figure 5). The C_{60} did not dissolve in PEG400DME with LiClO4. However, C_{60} anions could be dissolved in the above solvent.

The AC impedance measurements showed that the solution resistance of PEG400DME was about 100 times higher than that of an aqueous solution. This high solution resistance caused large peak-to-peak separations of the C_{60} redox reactions. In order to overcome this problem, CVs were recorded by using a GC microelectrode which helped to reduce the peak potential shift to a few mV (see Figure 6). The redox current for the C_{60}/C_{60}^{-} pair was approximately twice as large as that for other redox pairs including C_{60}^{2-}, C_{60}^{3-}, C_{60}^{4-}, and C_{60}^{5-}. Other supporting electrolytes such as $KClO_4$ and $NaClO_4$ were also used to investigate the electrochemical behavior of C_{60} in the PEG400DME. Of these three alkaline metal salt electrolytes, the C_{60} anions were most stable with $KClO_4$.

Raman spectroscopy of the C_{60} film was carried out by using a Kr^+ laser (647.1 nm) as the excitation source. A thin C_{60} film deposited on a thin-film silver electrode surface

was placed in an air-tight electrochemical cell filled with Ar gas, and Raman spectra were recorded using the back scattering mode. Several medium-to-strong Raman bands due to solid C_{60} were observed at 273-1566 cm^{-1} at the open circuit potential. The above results are consistent with that of a C_{60} film prepared in vacuum.[2] We found it difficult to observe the Raman spectra of C_{60} anions because the C_{60} films dissolved in PEG400DME/$LiClO_4$ solution when a negative potential was applied to the electrodes.

Conclusion

In-situ Raman spectroscopy was applied to characterize the passive films on Li electrode surfaces in several solvent/electrolyte systems including propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), polyethylene glycol 400 dimethyl ether (PEG400DME). Either $LiAsF_6$ or $LiClO_4$ was used as a supporting electrolyte. The Raman spectra recorded in solvent and supporting electrolyte systems such as DMC/$LiClO_4$, PC/$LiClO_4$, and PEG400DME/$LiClO_4$ showed different Raman bands. The frequency of Raman bands was also affected by the charging and discharging potentials. The Raman bands from the passive film seemed to remain even when a positive potential was applied. The results suggested the structure of the passive films formed on the Li surface was affected by both the solvent and applied potential. The Li surface was much more reactive in DEC than the other solvents described above. However, the Li surface was stabilized by adding either methyl acetate (MA) or methyl formate (MF) to the DEC solution.

In-situ Raman spectroscopy of zinc electrode surfaces indicated the possible formation of ZnO and $Zn(OH)_2$ as a passive film with the application of passive potentials. However, due to the low sensitivity of the Raman spectrometer, the results presented here

are inconclusive. Further work is needed by using a more sensitive Raman spectrometer such as one interfaced with a microscope. This type of Raman spectrometer would also help in providing the detail structural information of the passive films formed on the Li electrode in different solvent/electrolyte systems.

References

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2. D. Bethune, G. Meijer, N. Tang, and H. Rosen, *Chem. Phys. Letters, 174,* 219 (1990).

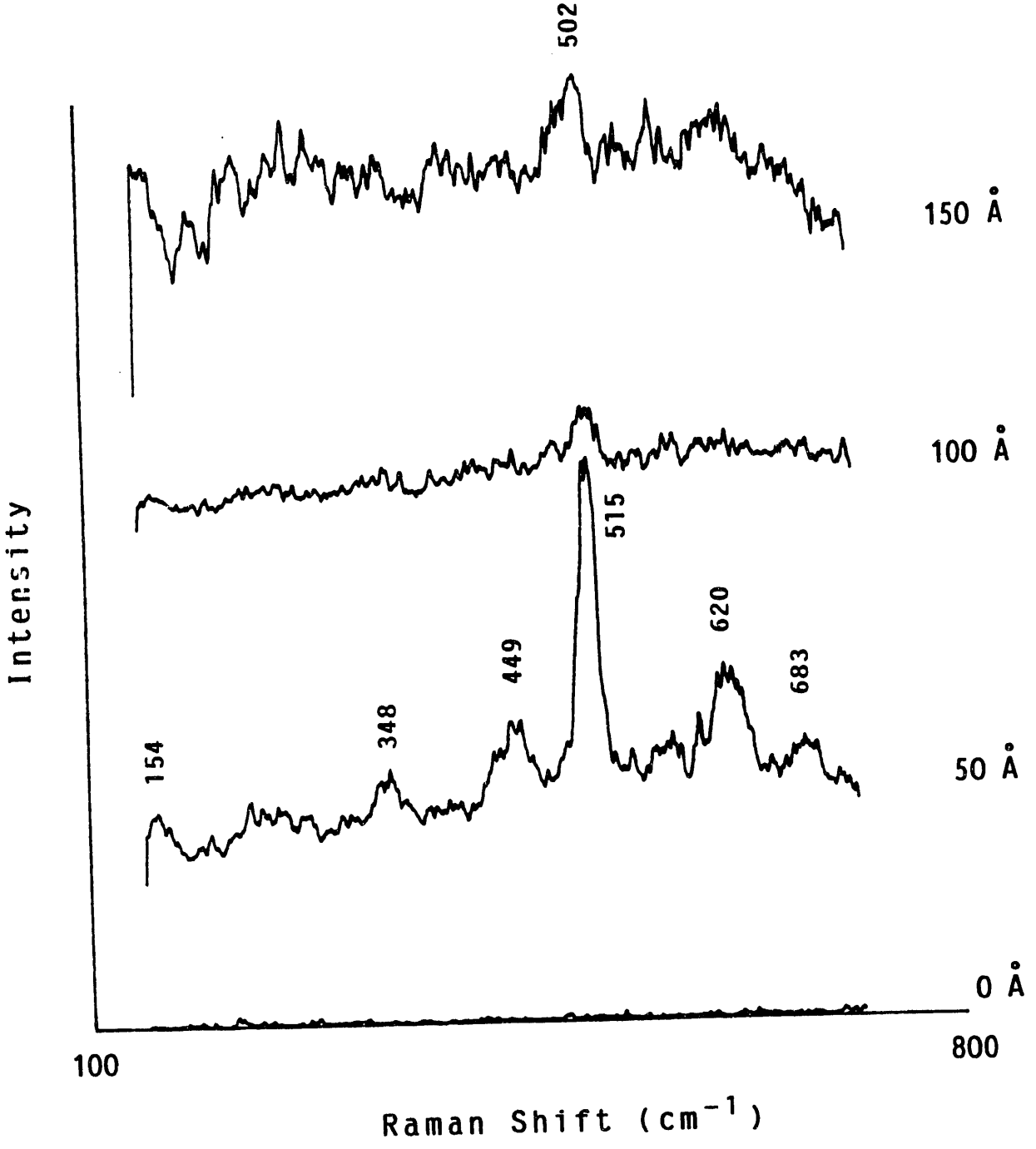

Figure 1a. Raman spectra (100-800 cm^{-1} region) at thin film Ag electrode after deposition of Li films in DMC/1 M $LiClO_4$, λ_{ex} = 514.5 nm - 150 mW

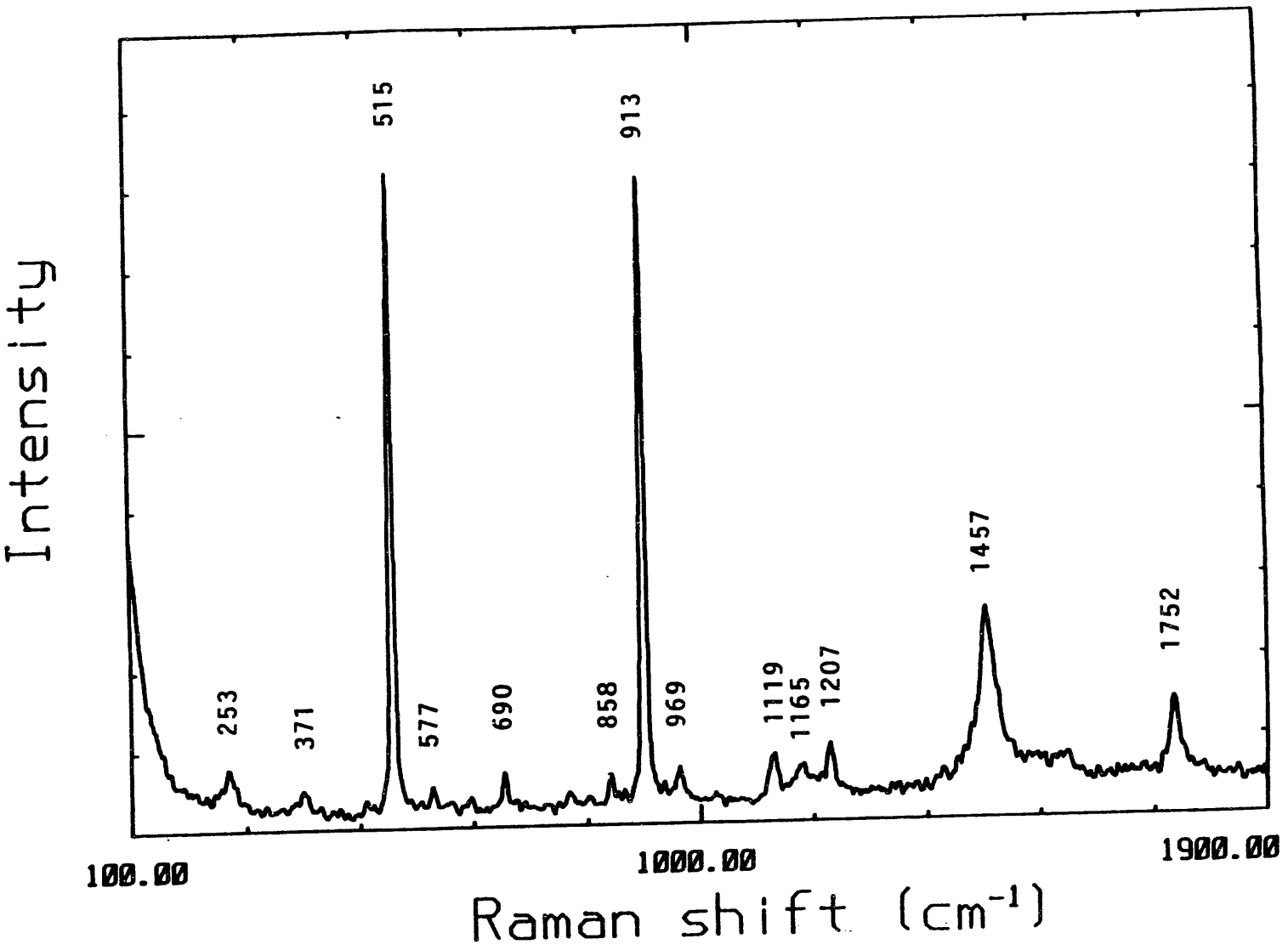

Figure 1b. Raman spectrum of DMC in quartz tube. λ_{ex} = 514.5 nm - 150 nm

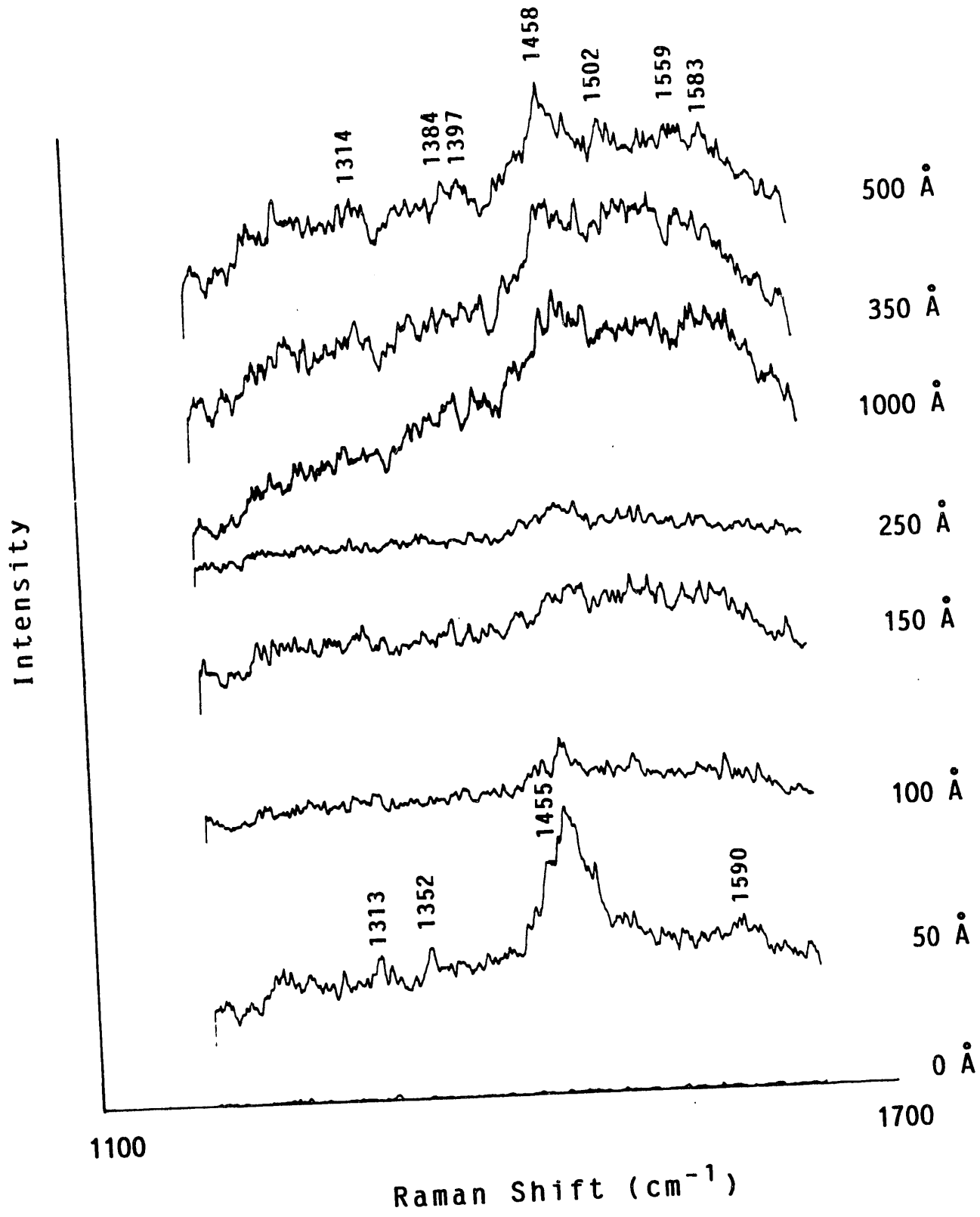

Figure 2. Raman spectra (1100-1700 cm^{-1} region) of thin film Ag after the deposition of Li films in DMC/1M LiClO4.
λ_{ex} = 514.5 nm - 150 mW

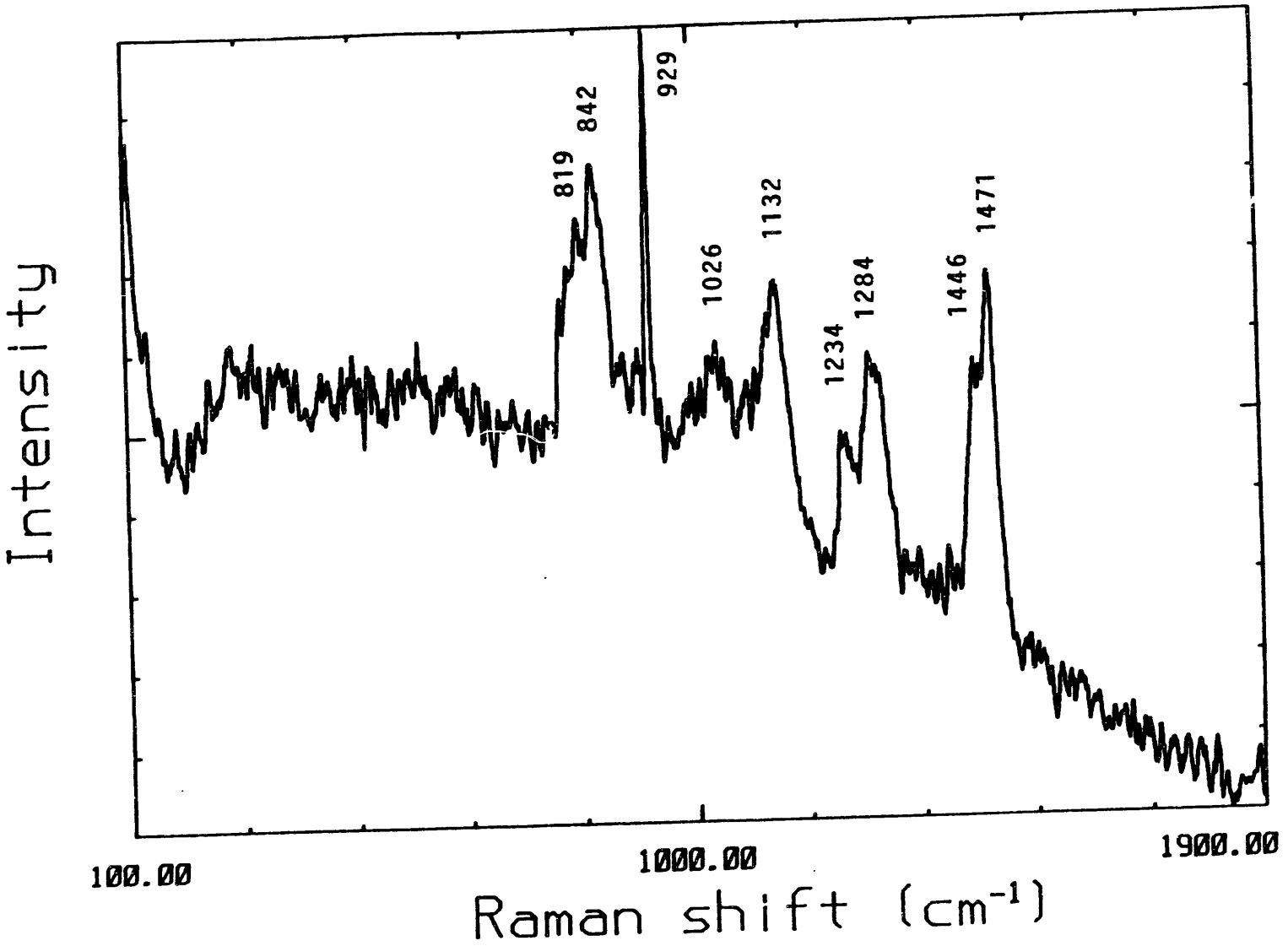

Figure 3. Raman spectrum (100-1900 cm^{-1} range) of thin film Ag in PEG400DME/0.5 M $LiClO_4$. No potential was applied to the electrode. λ_{ex} = 647.1 nm - 150 mW

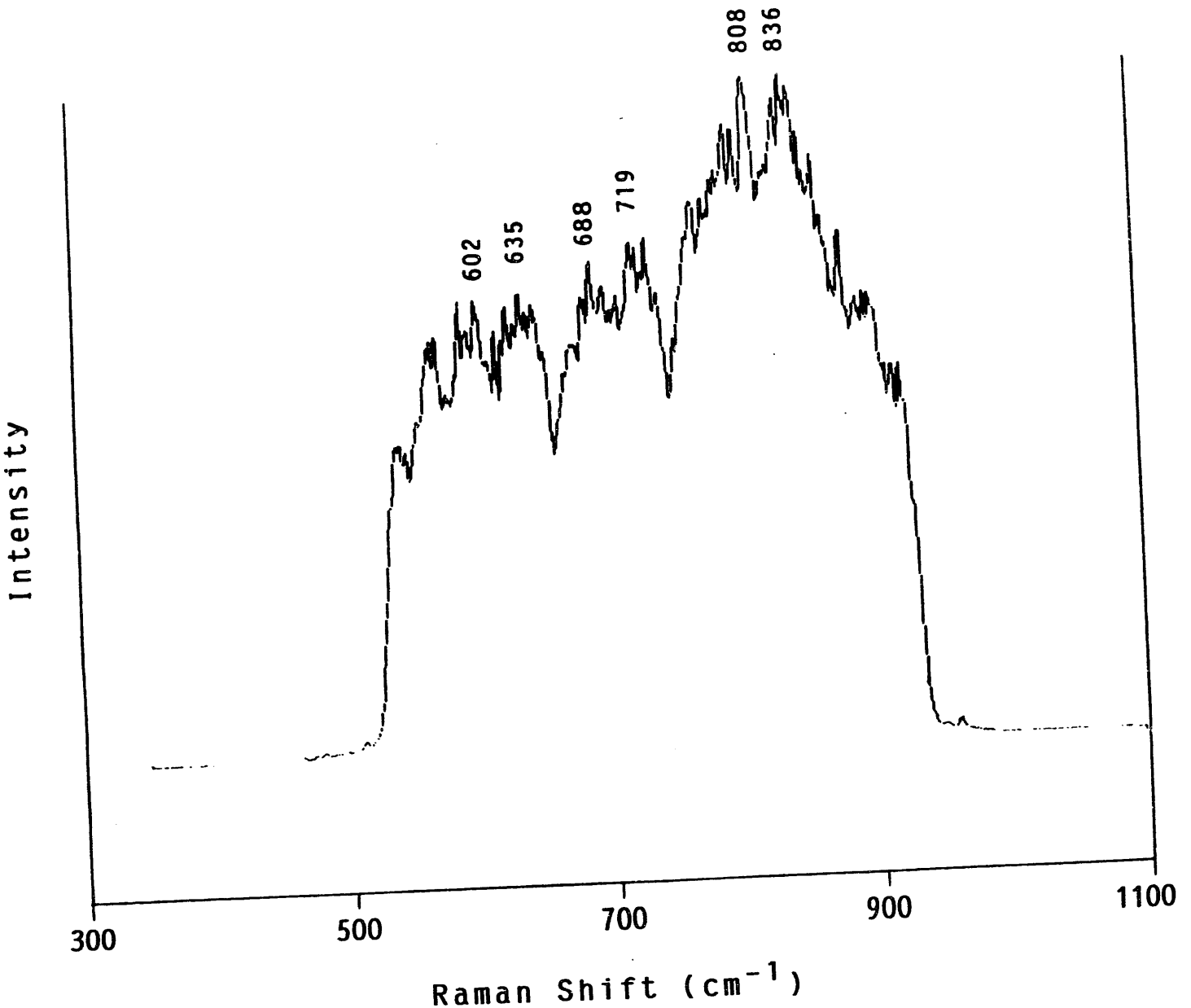

Figure 4. Raman spectrum (500-900 cm^{-1} range) of thin film Ag at -0.1 V (vs Li^+/Li) in PEG400DME/0.5 M $LiClO_4$. λ_{ex} = 647.1 nm - 150 mW

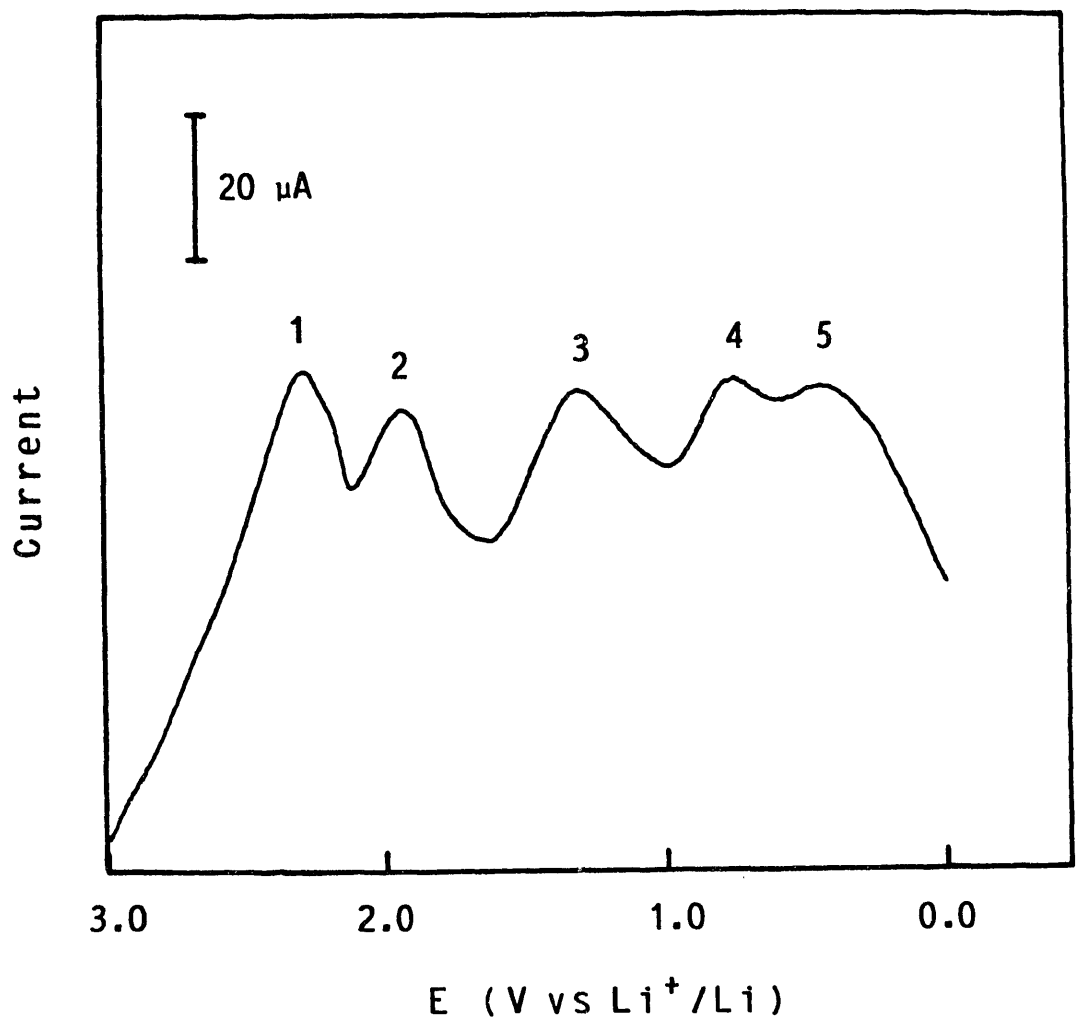

Figure 5. Linear sweep voltammogram at thin film C_{60} film on GC (3 mm dia) in PEG400DME/0.5 M $LiClO_4$. Scan rate: 100 mV/s

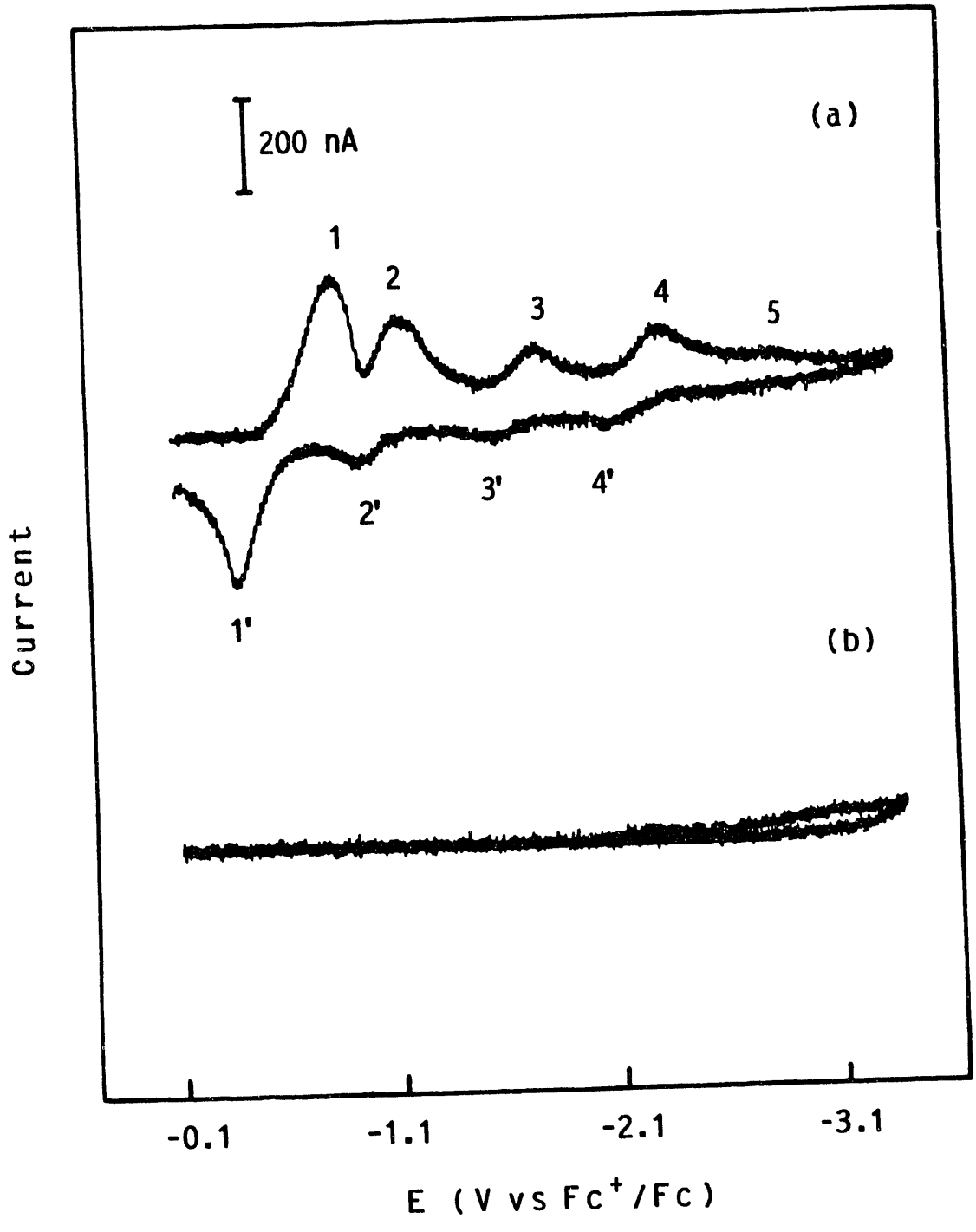

Figure 6. Cyclic voltammograms in PEG400DME/0.5 M $LiClO_4$ at (a) thin C_{60} film on GC (30 μm) electrode and (b) on bare GC (μm) electrode. Scan rate: 1 V/s

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