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Properties of a Carbon Negative Electrode in Completely Inorganic Thin Film Li-Ion
Batteries with a LiCoO_2 Positive Electrode

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Abstract

Completely inorganic thin film lithium ion battery cells have been prepared by vapor deposition processes (vacuum evaporation and sputtering). The negative and positive electrodes were films of disordered carbon and lithium cobalt oxide, respectively. The results of battery charging/discharging and other measurements (e.g., in-situ lithium chemical diffusion constant measurements for the carbon films) indicate that disordered carbon films have a relatively high reversible charge capacity, ($> 160 \text{ mC/cm}^2\text{-}\mu\text{m}$, and possibly higher than $360 \text{ mC/cm}^2\text{-}\mu\text{m}$, or > 296 and possibly 667 mAh/g , respectively, assuming the measured film density of 1.5 g/cm^3), and a lithium chemical diffusion constant at room temperature $\approx 10^{-9} \text{ cm}^2/\text{s}$. These results suggest that disordered carbon films should be good substitutes for metallic lithium in thin film rechargeable batteries.

Introduction

Currently, there exists a need for stable and affordable high energy and power density batteries for portable electrical and electronic equipment, and most importantly for powering electrical vehicles and for electrical power load leveling. Lithium-ion rocking-chair cells, that employ completely inorganic thin films, including thin film high voltage transition metal oxide positive electrodes (cathodes) are attractive candidates for rechargeable batteries. This is for several reasons among which are: (i) their potentially high energy and power densities (gravimetric and volumetric); (ii) the high probability for economically producing sequentially deposited bipolar stacks of series-connected cells, and thereby obtaining relatively high voltage batteries; and (iii) their potential to be stable for thousands of deep charge-discharge cycles, especially because of the proven or anticipated wide electrochemical stability range for thin film inorganic electrolytes [1,2].

For reasons of safety, materials availability, and practical manufacturing, it is desirable to use an insertion anode (negative electrode) rather than lithium metal. Carbon appears to be a good candidate. There are already available commercially LiCoO_2 (cathode)/C (anode) bulk rechargeable batteries [3] and, recently, it has been reported that a type of bulk disordered carbon has a relatively high charge capacity (approximately 680 mAh/g or $550 \text{ mC/cm}^2\text{-}\mu\text{m}$, assuming a bulk density of 2.25 g/cm^3) [4,5].

This paper is essentially a work-in-progress report on some of the properties of thin films of disordered carbon as employed in rocking-chair cells using a LiCoO_2 cathode. Although other LiMO_2 compounds (M = one or more of the several 3d transition metals) are strong contenders for the cathode, LiCoO_2 was chosen because of its being used commercially and because of our prior experience with it in electrochromic window cells [6]. The results to date suggest that disordered carbon films should be considered as good substitutes for lithium metal anodes in thin film batteries.

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Experimental Details

Lithium cobalt oxide (nominally LiCoO_2) films were prepared by rf sputtering. The deposition conditions were: 5 inch diameter target of stoichiometric LiCoO_2 , rf (13.56 MHz) power = 100 Watts, oxygen pressure = 10 mT, substrate to target distance = 7 cm, deposition rate = 130 nm/hr, and the substrates were at ambient temperature. The films were "Xray amorphous" and their density was approximately 3.7, as determined by a quartz crystal oscillator microbalance (mass) and a profilometer (thickness).

The electrolyte generally used was lithium phosphorous oxynitride (Lipon) [1]. It was prepared by reactive rf magnetron sputtering from a 2 inch target of Li_3PO_4 in a nitrogen atmosphere. The deposition conditions were: rf power was either 100 Watts or 150 Watts, nitrogen pressure = 15 mT, substrate to target distance = 15 cm, deposition rate (@ 150 Watts) \approx 75 nm/hr, and the substrates were at ambient temperature. The refractive index of the films was approximately 1.6 and their thicknesses were determined by both optical interference and profilometry measurements.

The carbon films were deposited by a controlled dc anodic arc process. Graphite electrodes were used for the anode and cathode, and the depositions were carried out in vacuum (pressure $< 2 \times 10^{-5}$ Torr). The anode was machined from a high purity rod of graphite, with its evaporation end diameter = 2.5 mm; and the cathode was a dome shaped graphite rod of 2.5 cm diameter 2.5 cm. The depositions were made using a dc lamp supply. The current was generally 35 A and the voltage was 20 V. The estimated current density at the anode during depositions was $> 1000 \text{ A/cm}^2$. Deposition rates exceeded 140 nm/s for substrate-anode distances of 5 cm and 35 nm/s for a 10 cm distance. The carbon film density was approximately 1.5, again determined by a quartz crystal oscillator microbalance (mass) and a profilometer (thickness). The films were nearly "Xray amorphous", with a broad peak at $2\theta = 23^\circ$ and a much smaller one at 42° (Figure 1), similar to that reported recently for bulk disordered carbon [5]; and they exhibited a predominance of sp^2 bonding as determined from Raman spectroscopy.

Metal films (Cr, Cu, Al, TiN) were deposited by thermal evaporation - either by electron beam heating (TiN) or by electrically heating a refractory metal boat (Cr, Cu, Al) - or by sputtering (TiN).

Three types of cells were prepared, but all three types were fabricated by sequential vacuum depositions, resulting in the structure: [(glass substrate)/(cathode metal current collector)/(positive electrode)/(electrolyte)/(negative electrode = carbon)/(anode metal current collector)]; and some cells were further sealed with a dielectric layer. The order of the depositions was purposely chosen to provide discharged cells and to avoid the problem of removing lithium from the carbon films before the LiCoO_2 deposition.

One type of cell, Type 1, employed a Tufts LiCoO_2 cathode followed by approximately 100 nm of sputter deposited LiNbO_3 and then was sent to Eveready for completion by depositing their lithium oxy-sulfide electrolyte and a lithium metal anode. Characterizations were then done at Eveready in a controlled atmosphere chamber. Type 2 cells were basically the same as type 3 as regards composition - i.e., both were [(metal)/(LiCoO_2)/(Lipon)/(C)/(metal)] cells. The major difference between the two types were that type 2 had unequal area electrodes, with the carbon electrodes being considerably smaller in area; this allowed us to deposit many anodes at once and insure that at least one cell was not shorted as a result of pinholes in the electrolyte.

Several type 3 cells employed secondary reference electrodes which were freshly deposited carbon layers on the Lipon electrolyte where it was covering only the glass substrate.

The carbon reference electrode was calibrated by measuring its potential ($\approx +2.1$ V) vs freshly deposited Li.

Measurements and Results

Shown in Table 1 is a summary of results from some of the measurements that were performed on LiCoO_2 and carbon films. Some of the measurements were done on metal/electrode bilayers. Others were done in-situ, using type 2 or type 3 cells.

For reference potential measurements, a battery-powered electrometer, (Keithley 602, with input resistance $\approx 10^{14} \Omega$), operating in a guarded mode, was utilized. The guarded mode allowed for stable, fast transient measurements). Galvanostatic and potentiostatic measurements were generally done using an EG&G PAR 263 potentiostat with computer control and data acquisition.

The chemical diffusion coefficient (\tilde{D}_{Li}) measurements for LiCoO_2 were made on bilayers in a wet cell using a non-aqueous electrolyte (lithium perchlorate in ethylene carbonate/propylene carbonate), and were done in-situ in the cells for carbon. Transient techniques similar to the GITT method [7,8] were utilized. In the case of carbon, an alternative technique was utilized: following a long low current charging/discharging current pulse (to obtain a quasi-equilibrium state of charge), a shorter but much higher current pulse was applied (short compared to the diffusion time, $t_d \approx L_d^2/\tilde{D}_{\text{Li}}$, L_d = electrode thickness). For times shorter than t_d the electrode potential (relative to a reference electrode) should decay as $t^{-0.5}$, and for times $\geq t_d$ it should decay as t^{-m} , where $m < 0.5$, since the excess Li^+ "reflects" from the electrode/metal boundary, slowing down the diffusion away from the electrode/electrolyte boundary. Thus, by monitoring the logarithm of the potential vs the logarithm of the time, one obtains a direct measure of t_d , namely where there is a breakpoint in the slope of the plot. This is illustrated in Figure 2. There is a breakpoint in the slope at approximately 220 ms after the onset of the pulse. The carbon layer was approximately 150 nm thick and therefore $\tilde{D}_{\text{Li}} \approx 10^{-9} \text{ cm}^2/\text{s}$.

Type 1 cells (LiCoO_2/Li) were used to obtain independent charging/discharging measurements for LiCoO_2 . Out of 250 cycles, during the first 25 cycles plus during four other sets of 3 to 5 consecutive cycles, or during a total of 40 cycles, the LiCoO_2 films exhibited reversible charging/discharging of approximately 6 μAh . Cycles 5, 6, and 7 are shown in Figure 3. The films were approximately 110 nm thick and the cell area was 1 cm^2 . The reversible charge capacity therefore corresponded to $> 190 \text{ mC/cm}^2\text{-}\mu\text{m}$, or assuming a density of 3.7 g/cm^3 the capacity was $> 140 \text{ mAh/g}$.

Several type 2 cells (LiCoO_2/C) had their electrolyte layer deposited under less energetic conditions than for type 3 cells (also LiCoO_2/C). The second discharge and third charge half cycles are shown for one of the type 2 cells in Figure 4. The data were taken using a charging current density of $1 \mu\text{A/cm}^2$. The area of the carbon electrode was 0.05 cm^2 and its thickness was between 180 and 280 nm. Using the latter thickness, the reversible charge capacity was $> 160 \text{ mC/cm}^2\text{-}\mu\text{m}$ ($> 295 \text{ mAh/g}$ for a density of 1.5 g/cm^3), and for the former thickness, it was $> 250 \text{ mC/cm}^2\text{-}\mu\text{m}$ ($> 460 \text{ mAh/g}$ for a density of 1.5 g/cm^3). Several type 2 and type 3 cells exhibited short circuit current densities $> 1.0 \text{ mA/cm}^2$, and on more than one occasion $> 1.5 \text{ mA/cm}^2$. The short circuit current density for one type 3 cell was $> 500 \mu\text{A/cm}^2$ for longer than 5 seconds. These short circuit tests were done with charged cells open circuit potentials $\geq 3 \text{ V}$. One type 2 cell was first charged to $400 \text{ mC/cm}^2\text{-}\mu\text{m}$ and $360 \text{ mC/cm}^2\text{-}\mu\text{m}$ could be removed, but only with

a high discharging voltage. On the second charge 360 mC/cm²-μm could be reinserted into the carbon layer. This corresponds to a reversible charge capacity of > 660 mAh/g assuming the measured density of 1.5 g/cm³ for the carbon films.

On a number of occasions large stress changes that occurred during charging/discharging led to stress-relief cracking of the top metal film. In previous studies of LiCoO₂ films, we have measured changes of stress due to changes in lithiation as large as 2 to 4 GPa. As-deposited films generally exhibited an internal stress of approximately -2 GPa (compressive), and upon delithiation the stress became more tensile, sometimes reaching +2 GPa. To date only as-deposited stress measurements have been made on carbon films, and they exhibit a (compressive) stress of approximately - 0.8 GPa. The internal stress measurements were made on films that were deposited on thin cover glass substrates, using an optical technique [9] to determine the induced substrate curvature.

Further Discussion and Conclusions

Although more research is needed on cells employing carbon film anodes and LiMO₂ film cathodes (M = 3d transition metal(s)), the results to date suggest the following conclusions:

(i) The electrolyte deposition process probably adversely affects the kinetics of LiCoO₂/C cells. This is likely due to the formation of a very low electron and lithium ion conductivity region either within the LiCoO₂ layer itself and/or between it and the electrolyte. This appears to be a process parameter effect, (principally sputter power density), and not an intrinsic LiCoO₂ effect. The evidence for this is the difference between the charging/discharging behavior of type 3 cells (poor kinetics - very high overpotentials on discharge) compared to type 1 and 2 cells, both of which had a buffer electrolyte layer (100 nm of LiNbO₃ for the type 1 cells and approximately 200 nm of a 100 W Lipon for the type 2 cells). One might speculate that there is a plasma induced reaction between Lipon and LiCoO₂ which affects the transition region. This needs to be investigated further.

(ii) The electrolyte deposition also appears to cause a change in the density of states and/or a heavy lithiation (chemical reduction) of the underlying LiCoO₂ layer since the chemical potential of the LiCoO₂ is lowered considerably, from being > 2.5 to 3.5 Volts (vs Li) for as-deposited films to < 2 Volts after the electrolyte deposition. This may be directly associated with item (i), although the chemical potential has been found to be relatively low (2 to 2.5 V) for LiCoO₂ in as-deposited type 2 cells, yet they exhibited satisfactory room temperature kinetics. This, too, is very likely a process parameter effect, associated with changes in the microstructure of disordered LiCoO₂.

(iii) In addition to items (i) and (ii), the high overpotentials associated with discharging some types 2 and 3 cells, and the origin of the often observed loss of first charge capacity in disordered carbon, might be due to difficulty with ionizing covalent lithium, Li₂, which Sato et al. proposed as being stored between carbon planes and thus served as the source of the high charge capacity they observed for their disordered carbon [4]. It is also conceivable that some of the lithium in the carbon half cell might be irreversibly lost during the first charging by chemical reactions (e.g., by oxidation or alloying with the metal current collectors).

(iv) The carbon films are quite rough. Scanning tunneling microscope (STM) images of the films (Figure 5) indicate a peak to peak roughness of approximately 30nm with an rms roughness approximately 4-5 nm. Such roughness could adversely affect the integrity of subsequent sequentially deposited cells (especially as regards obtaining shorts-free electrolyte

layers) in high voltage batteries. Hence, for such batteries, it will be important to modify the deposition process so as to yield low roughness carbon layers.

(v) The reversible charge capacity of both LiCoO_2 films ($>190 \text{ mC/cm}^2\text{-}\mu\text{m}$) and C films, ($>160 \text{ mC/cm}^2\text{-}\mu\text{m}$ and possibly $> 360 \text{ mC/cm}^2\text{-}\mu\text{m}$), are satisfactory for high energy and power density batteries. However, there might be a significant amount of relatively low activity lithium in the carbon films, which could account for the high overpotential discharge characteristics of the cell which exhibited a reversible charge capacity of $360 \text{ mC/cm}^2\text{-}\mu\text{m}$.

(vi) Disordered carbon films have a useful lithium diffusion coefficient ($\approx 10^{-9} \text{ cm}^2/\text{s}$) possibly because of orientational disorder (random orientation of transport planes); and this coupled with their apparently high charge capacity, their relatively low charge state voltage ($< 0.5 \text{ V}$ vs lithium metal), the ready availability of carbon, and the relative ease with which one can rapidly and economically deposit them, make such films very attractive candidates for thin film anodes in rocking chair cells that employ LiMO_2 cathodes ($M = 3d$ transition metal, such as Co).

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Property	Lithium Cobalt Oxide	Carbon	Measurement(s)
Li diffusion coefficient \tilde{D}_L , (cm ² /s)	$\approx 10^{-12}$ - 10^{-11} (in bi-layer)	$\approx 10^{-10}$ or greater (in cell)	Transient
Charge capacity (mC/cm ² - μ m)	> 190	≈ 160 (possibly > 360)	V(q) (galvanostatic)
Mass density (g/cm ³)	≈ 3.7	≈ 1.5	Quartz oscillator-mass Profilometer-thick
V(q) (V vs Li)	2.2 to 4.2 (type 1 cell)	< 0.5 to > 2.0 (cells)	Galvanostat/Potentiostat Electrometer
Structure	Xray "amorphous"	2 θ peaks @ 23° & 42°, with sp ² bonding	Xray diffraction & Raman (for C)
Stress/Stress Change (GPa)	-3/less compressive ($\approx +2$) with [Li] \downarrow	-0.8/changes not yet measured	Substrate curvature
J _{sc} (mA/cm ²)	≈ 1.5	≈ 1.5	Cell @ V _{oc} ≈ 3.3 V

Table 1. Summary of some measured properties of films used in this study.

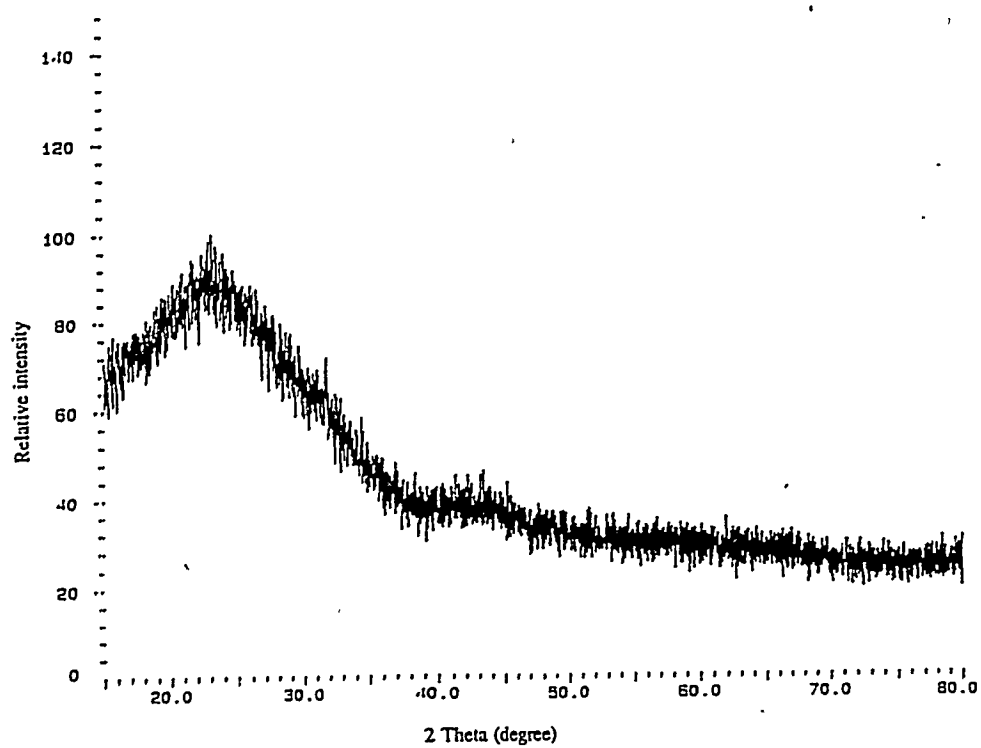


Figure 1. Xray diffraction pattern (Cu target) for carbon film deposited by anodic arc deposition process.

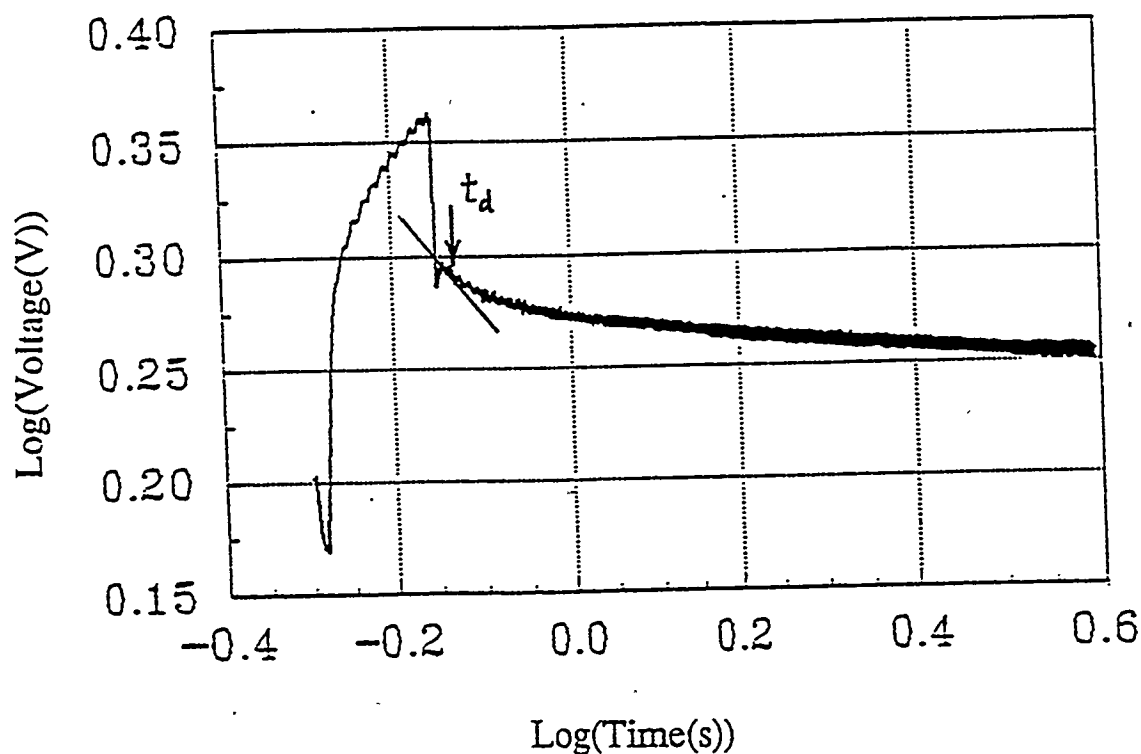


Figure 2. Carbon layer transient voltage compared to a carbon secondary reference electrode potential during and following a $50 \mu\text{A}$ current pulse (of approximately 178 ms duration). Note the breakpoint in slope from -0.5 to $-m$ ($m < 0.5$) at approximately 220 ms. Therefore, $t_{\text{diffusion}} = 220 \text{ ms}$, and since the layer is approximately 150 nm thick, the diffusion coefficient is approximately $10^{-9} \text{ cm}^2/\text{s}$.

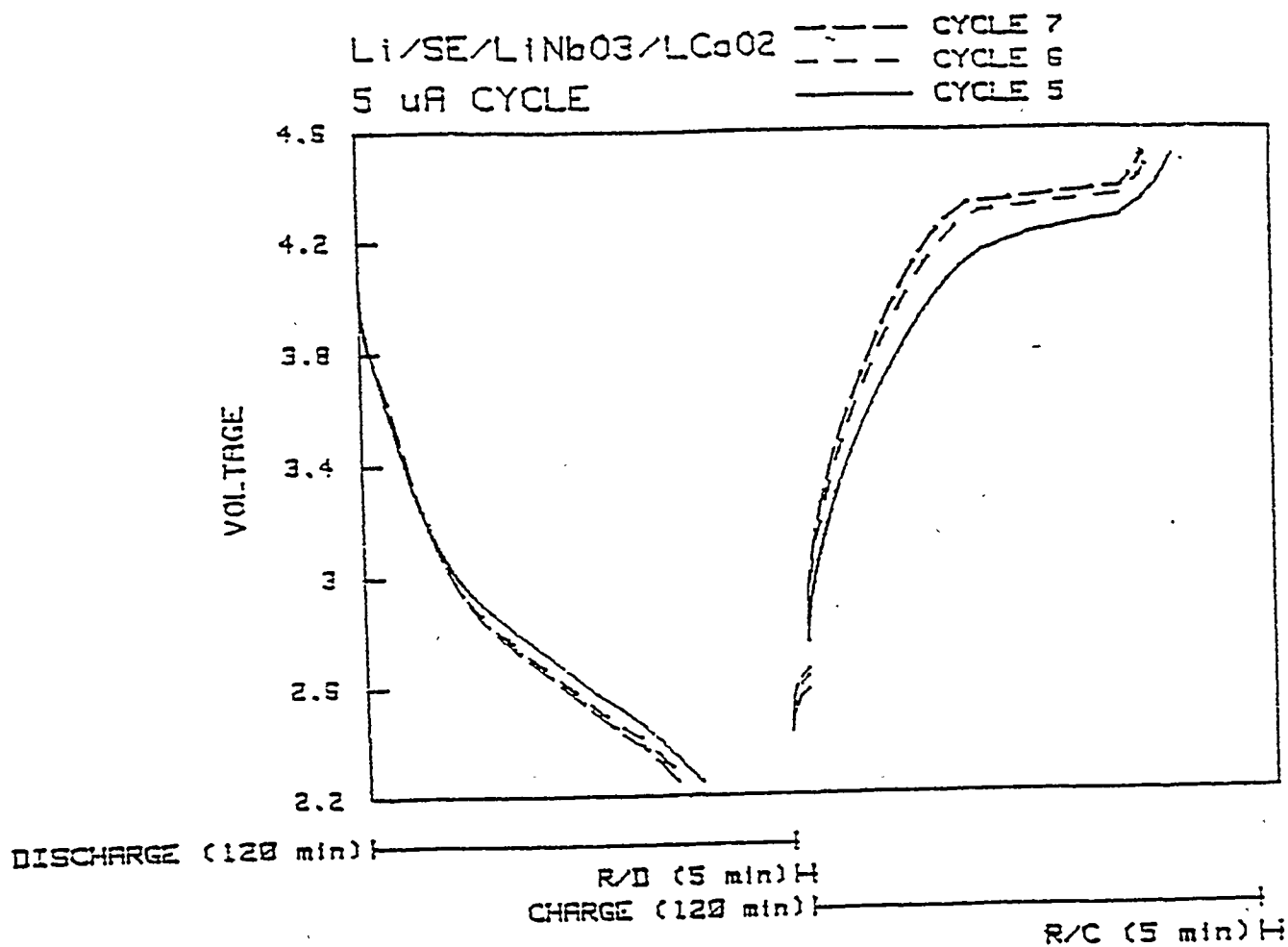


Figure 3. Charge and discharge cycles 5-7 for a type 1 cell (LiCoO₂/solid electrolyte/Li). Area = 1 cm². LiCoO₂ thickness \approx 110 nm. Current density = 5 μ A/cm².

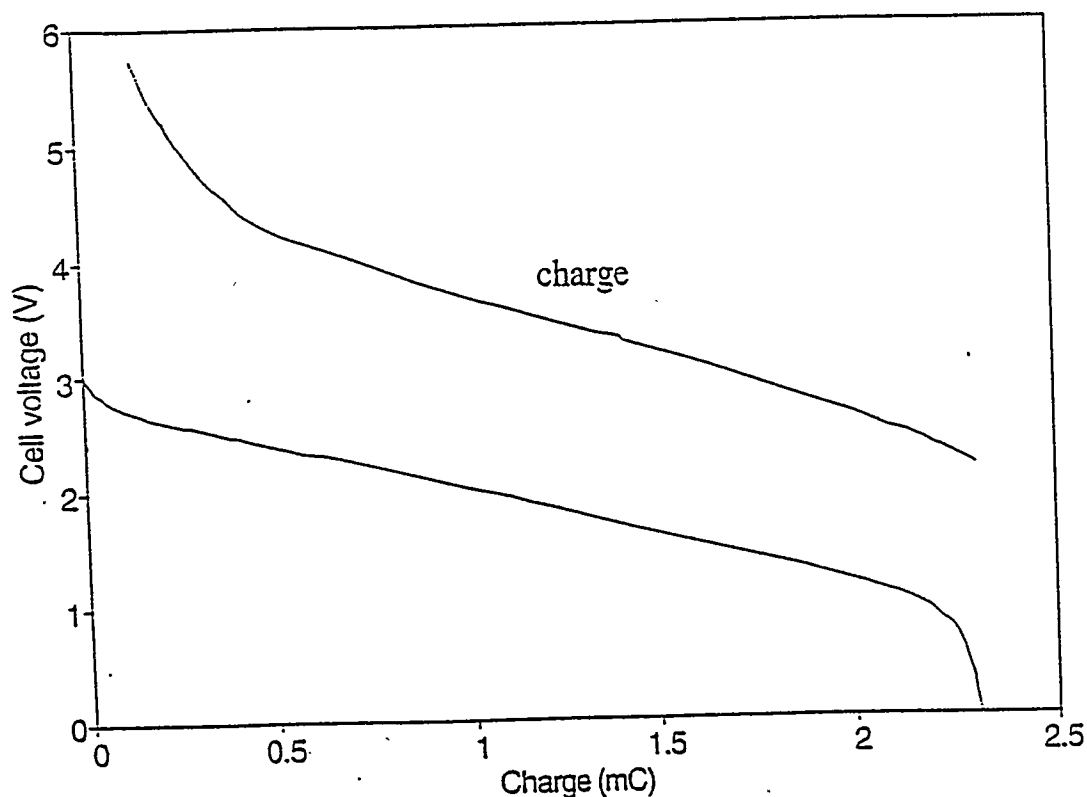


Figure 4. Third charge-discharge cycle for a type 2 cell ($\text{LiCoO}_2/\text{Lipon}/\text{C}$). C electrode area = 0.05 cm^2 . Carbon layer thickness between 180 and 280 nm. Current density = $1 \mu\text{A}/\text{cm}^2$.

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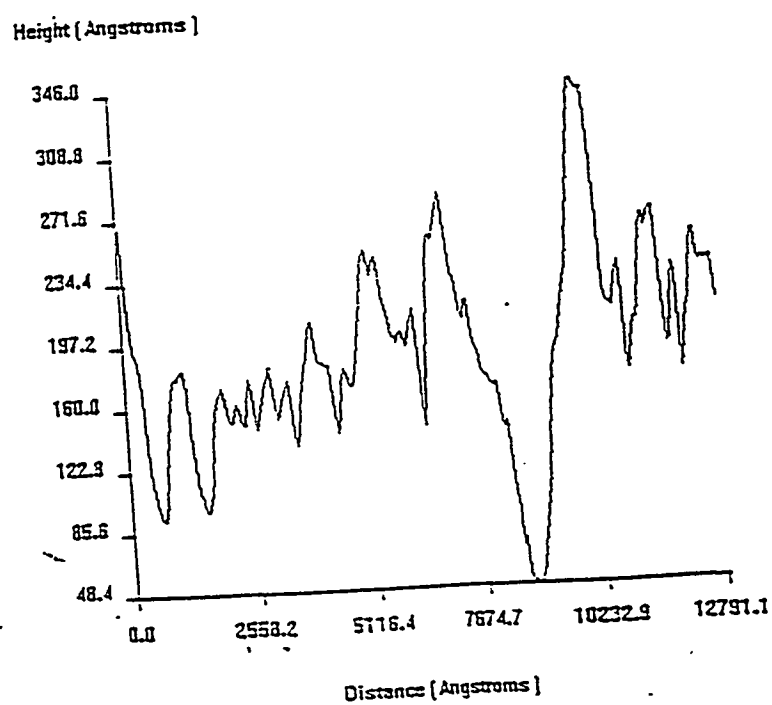
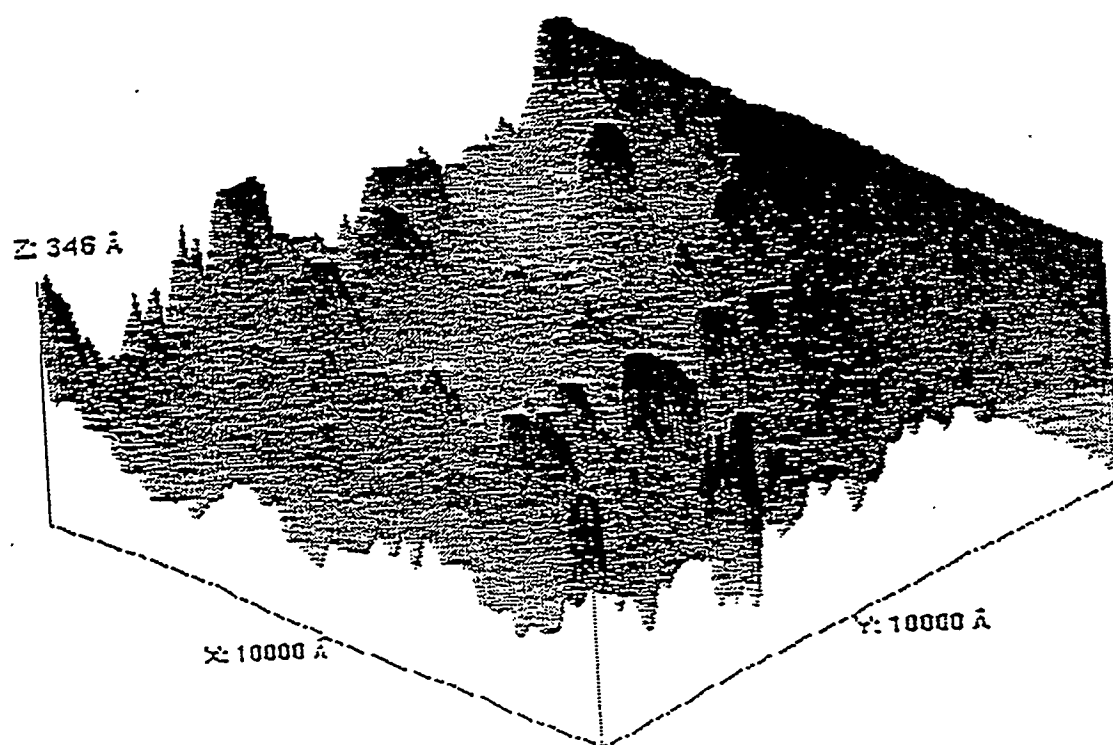


Figure 5. Scanning tunneling microscope image of anodic-arc deposited carbon film with diagonal cross-section. This image was obtained with a Burleigh Personal STM, using a Pt-Ir probe.