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**IN-SITU FT-IR SPECTROELECTROCHEMICAL
IDENTIFICATION OF PROCESSES
AT SOLID ELECTRODES**

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External reflection FT-IR spectroscopy was used for the elucidation of oxide thin film electrodes. The in-situ FT-IR spectroelectrochemical measurements allowed direct monitoring of the electrode processes without removing the electrode from the electrochemical environment. A FT-IR spectroelectrochemical cell was designed, which allowed easy exchange and adjustment of the working electrode. Intercalation and deintercalation processes of Li⁺ ions from an aprotic electrolyte in and out of the layered Li_{0.99}Co_{1.01}O₂ oxide thin film on Pt substrate, were investigated by in-situ subtractive normalized interfacial FT-IR technique (SNIFTIR). The reflection-absorption FT-IR spectra were obtained at potentiodynamic conditions at various electrode potentials ranging from -1.0 V to +1.4 V vs. a modified Ag/AgCl. Investigation of a Li_{0.99}Co_{1.01}O₂ oxide thin film deposited on Pt substrate showed that in deintercalation/intercalation processes of Li⁺ ions reversible structural and electronic changes in the electrode material appeared.

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Introduction

In the investigation of electrode processes, electrochemical measurements have been widely used for many years. However, these measurements provide no direct information on the identity of species at the electrode/electrolyte interface, their orientations, the nature of attachment on the surface, and the film thickness. Therefore, electrochemists are borrowing increasingly from the "*ex-situ*" and "*in-situ*" techniques recently developed in other areas of surface science, in order to obtain vital data on the electronic and molecular structure of the electrode material and electrode/electrolyte interface. The main drawback of the "*ex-situ*" techniques is the necessity to remove the electrode from the electrochemical environment. This would be eliminated if the electrode surface could be observed and characterized "*in-situ*".

The infrared external reflection spectroscopy, also known as reflection-absorption spectroscopy, has proven to be more than appropriate in "*in-situ*" and real-time observation of solid surfaces in liquid media. For this reason, this technique is becoming, with appropriate equipment, widely employed in the investigation of electrode processes. The infrared external reflection spectra of thin films on bulk electronically conducting substrates having a thickness much smaller than the wavelength of the incident radiation are readily recorded at the oblique incidence of the IR radiation on the surface of the film [1]. The early beginning of the reflection-absorption method was when Berreman showed that in thin cubic crystal films a strong absorption band also occurs at the frequency of polar longitudinal optical modes (LO) of long wavelength when the radiation is not incident normal to the surface of the film [2]. Later on, Greenler convincingly explained the increase in sensitivity at high incidence angles of p-polarized light on the substrate with the film [3]. For a quantitative analysis of the reflection spectra of thin films on solid surfaces, McIntyre and Aspens formulated a linear-approximation theory which has greatly simplified the theoretical treatment [4].

When solid electrodes are investigated in absorbing liquid media, strong IR absorption of the liquid interferes with the observation of faint signals of the surface species [1]. To obtain adequate transmission of IR light, the thickness of the solution layer must be a few micrometers or less [5]. We are then obliged to measure difference spectra, subtracting appropriate reference spectra from the sample spectra, when information about molecules in direct contact with the substrate is desired. For that reason, the subtractive normalized interfacial FT-IR spectroscopy (SNIFTIRS) is frequently used for observation of electrode surfaces [1,5-8]. Investigations of thin film oxides have demonstrated that the SNIFTIRS technique can be adapted to cope with the irreversible processes commonly observed in corrosion and thin oxide film formation [8-9]. The technique is also appropriate for the study of surface films formed on lithium and other conductive substrates in aprotic systems [10,11]. They are superior to

aqueous systems, since the absorptions of nonaqueous solvents are generally weaker than those of water. Therefore, a solution layer as thick as 50 μm may be used in the SNIFTIR observations [1].

In this paper we present the basic optical effects leading to the appearance of absorption bands in the reflection-absorption FT-IR spectra (external reflectance mode), an improved IR spectroelectrochemical cell design and the results obtained from the investigation of intercalation and deintercalation processes of Li^+ ions in and out of the Li_xCoO_2 ($0 < x < 1$) thin film deposited on a Pt substrate. Structural changes of the Li_xCoO_2 ($0 < x < 1$) film and the liquid layer of 1 M LiSO_3CF_3 in PC (Li triflate in propylene carbonate) electrolyte near the electrode surface were observed and discussed. Layered Li_xCoO_2 ($0 < x < 1$) with rhombohedral ($R\bar{3}m$) crystal structure is an extremely important material in battery industry [12] and a promising anodic counter electrode in electrochromic devices with WO_3 films [13]. The results reported here will elucidate the intercalation and deintercalation mechanisms of Li^+ ions and the accompanying structural and electronic changes in the film and in the layer of electrolyte near the film surface.

Infrared External Reflection Spectroscopy

Optical effects

Infrared external reflection spectroscopy has been used extensively in the study of thin films on conductive substrates. To understand the nature of the absorption or a decrease of reflection in a thin film on a conducting substrate, it is necessary to know how the IR radiation interacts with the electrode material.

To explain this, the three-layer system will be used, as it is shown in Fig. 1, which is present also in the spectroelectrochemical cell. Such a system consists of a thin film (e.g., adsorbed species, oxide film) on a conductive substrate (e.g., metal, ITO/glass-indium oxide film doped with tin on glass substrate, FTO/glass-tin oxide film doped with fluorine on glass substrate) and above the film there is air or a layer of liquid electrolyte. On a highly reflecting substrate the incident IR wave combines with the reflected wave of approximately equal strength, producing a standing wave with the node at the substrate surface [1]. The strength of the standing wave at the surface changes significantly depending on the polarization state of the incident IR beam and the angle of incidence. The phase shift for the component of the electric vector, typical for *s*-polarized light $E_{\perp 1}^+$, which is perpendicular to the plane of the incidence, is close to 180° for all angles of incidence [3]. In Fig. 2a the geometry of the electric vectors near the surface for the incident and reflected wave of *s*-polarized IR beam is presented. These vectors will very nearly cancel each other in the node on the substrate surface for all angles of incidence,

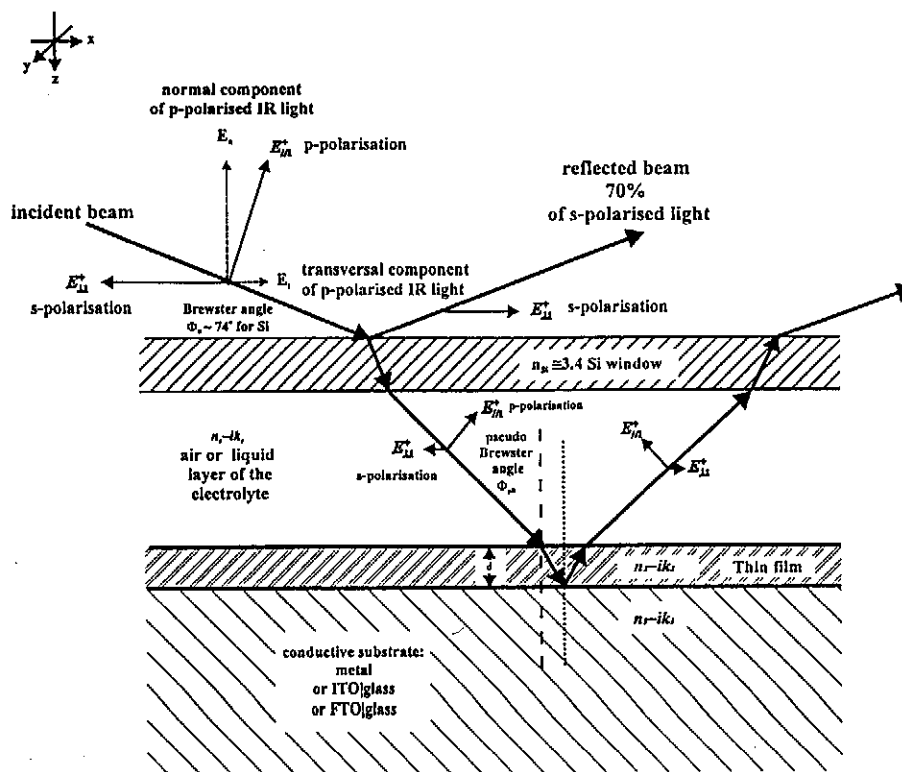


Fig. 1 Schematic presentation of the layers in an *in-situ* FT-IR spectroelectrochemical cell with the optical path of IR beam

leading us to the conclusion that we should expect little absorption from a layer on the conductive surface with reflection of light polarized perpendicularly to the plane of incidence.

The phase shift for the component polarized parallel to the plane of incidence or so called p-polarization, E_{\parallel}^+ , changes rapidly at high angles of incidence [3]. In Fig. 2b again the geometry of the electric vectors at a high angle of incidence is presented, where the phase shift upon reflection in the node on the surface is 90° . The vector addition of incident and reflected waves at the surface of the substrate should give rise to an elliptical standing wave with a sizable component of the electric vector E_n normal to the substrate surface. This means that those molecular or crystal lattice vibrations whose change in electric dipole is normal to the surface of the film (these are longitudinal optical modes, LO) will be strongly excited, giving rise to absorption bands in the IR reflection-absorption spectrum, whereas the parallel components (transversal optical modes, TO) will produce absorption of negligible intensity. Thus, surface charges produced by the normal component of the electric field generate a resonance, also called Berreman effect, at the LO

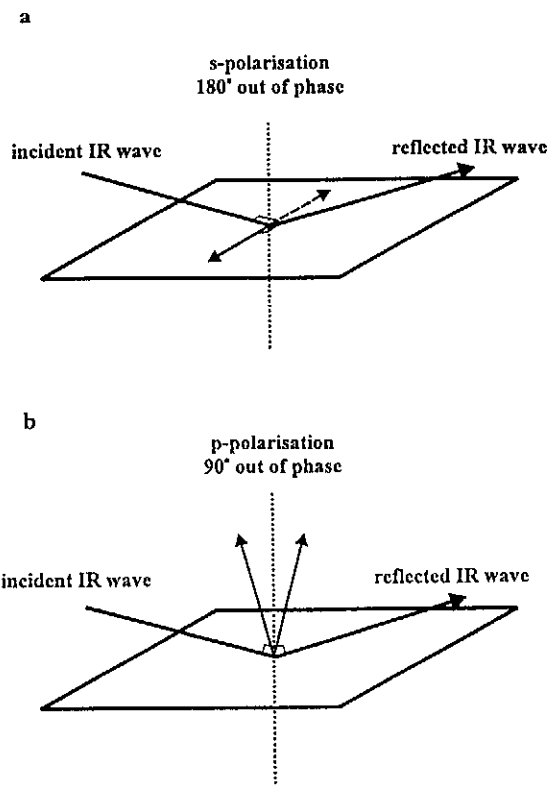


Fig. 2 Schematic presentation of the geometry of the electric vectors near the substrate surface for the incident and reflected wave of *s*-polarized IR beam (a) and *p*-polarized IR beam (b)

frequency [2].

Also in the case of free electrons which are present in a conducting substrate a dipole vibrating normally to the surface of the substrate gives rise to an image dipole which is parallel to the dipole of the surface species (Fig. 3) [14]. Thus the resonant absorption occurs at the frequency of the plasmon. On the contrary, the dipole vibrating parallel to the metal surface generates an image dipole which is oriented antiparallel, resulting in the compensation of the dynamic dipole moment [1].

Method of Measurements

When solid electrodes are investigated in absorbing liquid media, strong IR absorption of the liquid interferes with the observation of faint signals of the surface species. The polarization modulation and electrode potential modulation are effective methods for minimizing such interference and are often applied to the "*in-situ*" observation on bare and oxide-covered electronically conductive

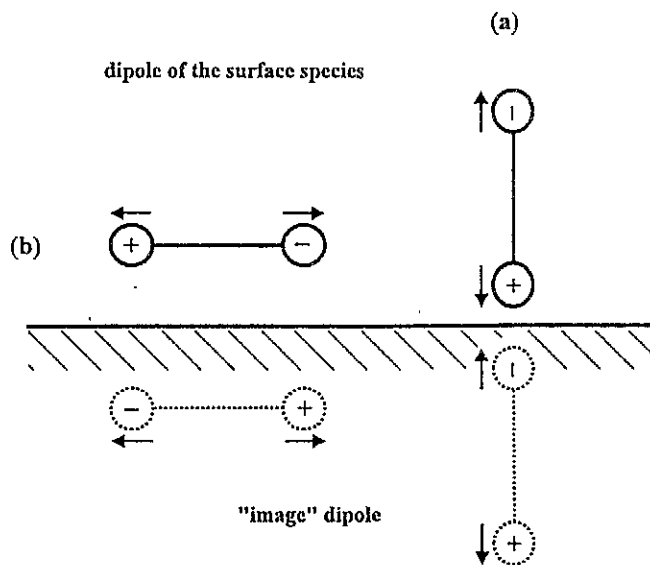


Fig. 3 (a) Schematic presentation of the changes during the vibration of a dipole oriented parallel to the surface of the conductive substrate; the "image" dipole change is in the opposite direction to the dipole of the surface species.
 (b) Schematic presentation of the changes during the vibration of a dipole oriented perpendicular to the surface of the conductive substrate; the "image" dipole change is in the same direction as the dipole change of the surface species

surfaces [1]. The electrode potential method provides, in real time, the change in the IR spectra of surface species, arising from the electrode potential sweep. In the observation of solid/liquid interfaces, however, external reflection IR technique usually provides information about interface layers of about 100 nm or more in thickness in addition to recording the signals from the bulk [1]. To obtain adequate transmission of IR light, the thickness of the solution layer must be a few micrometers or less [5]. We are then obliged to measure difference spectra, subtracting appropriate reference spectra from the sample spectra, when information about molecules in direct contact with the substrate is desired. For that reason, the subtractive normalized interfacial FT-IR spectroscopy (SNIFTIRS) is frequently used for observation of electrode surfaces [1,5-10]. A single beam spectrum which is used as a background, is usually obtained from the reflection of IR light on the cell, which was filled with the electrolyte and the bare substrate. Reflectance spectra are derived by subtracting this single beam spectrum from all further measured single beam spectra, which are obtained under the same conditions but, for example, with the sample species or the thin oxide film on the substrate. The normalized spectra $\Delta R/R$ are expressed by Eq. (1), by subtracting reference spectrum R_{E_1} obtained at the

reference potential E_i ($i = 1$) from single beam spectra $R_{E_{i+1}}$ recorded at different electrode potentials E_{i+1} ($i = 1, \dots, n$).

$$\frac{\Delta R}{R} = \frac{R_{E_{i+1}} - R_{E_i}}{R_{E_i}} \quad i = 1, \dots, n \quad (1)$$

In the normalized spectra $\Delta R/R$, both positive and negative bands can appear, which correspond to species present in a greater amount at the E_i and E_{i+1} potential, respectively.

***In-situ* Spectroelectrochemical Equipment**

An *in-situ* observation of electrode processes requires the combination of electrochemical and FT-IR reflection methods which are combined in a specially designed spectroelectrochemical cell which is shown in Fig. 4a.

The working thin film/metal or thin film/ITO/glass (or also thin film/FTO)/glass) electrode is put in a cylindrically shaped Teflon holder, which is moving forth and back, with the help of a micrometer screw, in a cylindrical teflon housing in the direction perpendicular to the film surface (or covering window). This enables an exact positioning of the electrode in the cell. The parallelism and variable reproducible adjustment of the distance between the surface of the working electrode and the covering window is ascertained by pushing the working electrode, as close as possible, to the covering window (zero position) and then shifting it for a controlled distance from the window. The optimum distance between the infrared transparent window and the electrode surface is critical because of the absorption of electrolyte which can significantly decrease the intensity of reflected light. Too small distances could considerably disturb electro-chemical reactions, due to an enhanced diffusion resistance [9]. The optimum distance between the working electrode and window is adjusted by measuring the intensity of the interferogram. The cell is covered with a flat silicon window which is transparent in the mid- and far- infrared regions and possesses high chemical inertness. The main drawback of this material is its opaqueness to visible light, therefore the electrode surface cannot be observed during cell alignment and measurement. In addition, the refractive index of silicon is high ($n_{Si} \approx 3.4$), giving rise to a high reflection loss of IR light [1]. For this reason, the infrared beam is incident at the Brewster angle ($\phi_B = 74^\circ$ for silicon) (see Fig. 1) on the covering window because p-polarized light, which interacts with the surface of the electrode, is totally refracted into the window upon incidence at the Brewster angle. The IR beam penetrates from the silicon/solution interface into the electrolyte layer at the pseudo-Brewster angle for absorbing solution [1], and the intensity of p-polarized light, therefore,

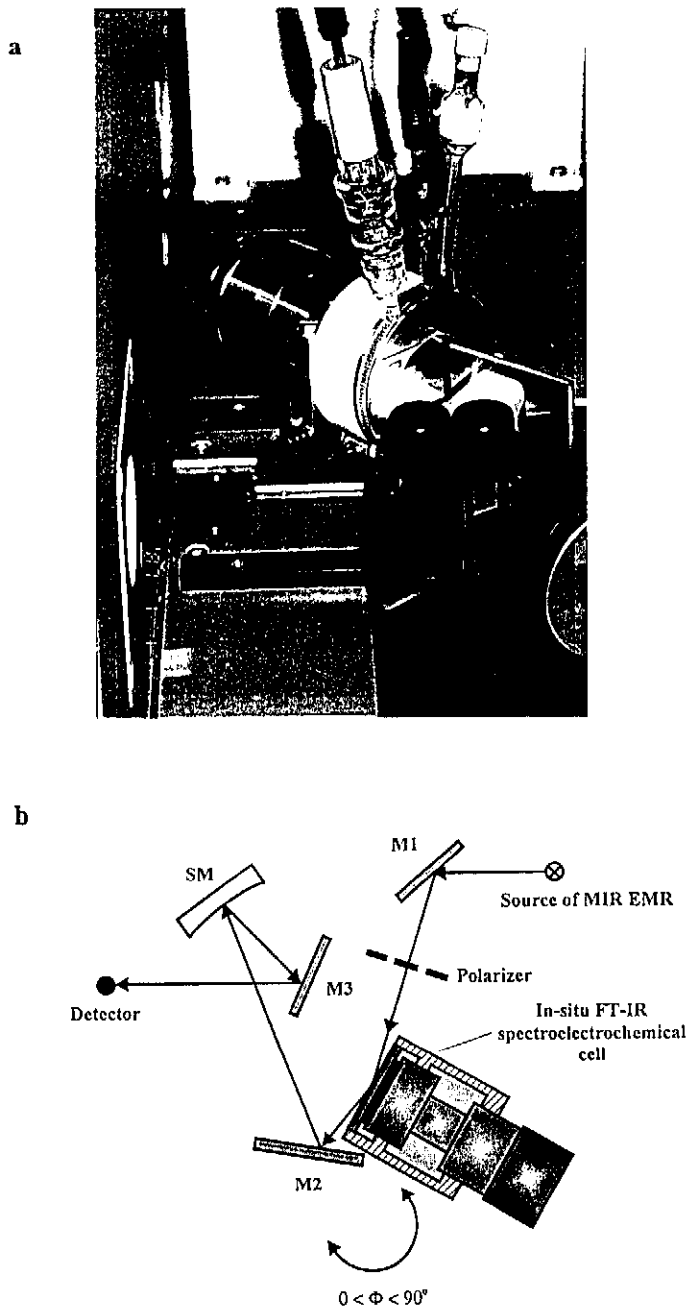


Fig. 4 (a) *In-situ* FT-IR spectroelectrochemical cell which was used for investigation of structural changes at solid electrodes
 (b) Schematic presentation of mounting of the spectroelectrochemical cell on an adjustable angle resolved probe stage in an external reflection attachment. (M1, M2 and M3 - plane mirrors, SM - spherical mirror)

is sizably reduced during transition through the cell. The reflectance of *s*-polarized light, which is of little use for the observation of the electrode surface, is about 70% on the silicon window at the Brewster angle. This component can be totally removed by the use of a polarizer.

The spectroelectrochemical cell was mounted on an adjustable angle resolved probe stage in an external reflection attachment purchased from Harrick Scientific Corporation. The mounting of the cell and the path of the infrared beam in this external reflection equipment is shown in Fig. 4b.

The working electrode consisted of a thin oxide film, deposited on both sides of a platinum sheet with dimensions of $5 \times 2.5 \times 0.3 \text{ cm}^3$, which served as a substrate. A high surface platinum grid in the shape of a circle, with a radius adjusted to the inner dimensions of the movable Teflon holder, served as a counter electrode in a three electrode arrangement. The reference electrode was connected *via* a Haber-Luggin capillary to the hollow Teflon holder, which served as an electrolyte compartment. The distance between the working electrode and the tip of the reference electrode was kept as small as possible. The reference Ag/AgCl electrode was modified, due to the aprotic media, by soaking the dry electrode in a saturated methanolic solution of LiCl; after that it was put into the salt bridge with 1 M LiSO_3CF_3 in PC. The standard potential of the modified Ag/AgCl electrode ($E_0 = +0.212 \text{ V vs. SHE}$) was determined from the potential difference against a saturated Ag/AgCl electrode ($E_0 = +0.197 \text{ V vs. SHE}$).

This spectroelectrochemical arrangement enables potentiostatic, galvanostatic and potentiodynamic investigations of thin film electrodes. Potentiodynamic measurements are limited by several factors: the thin layer of the electrolyte must be applied between the working electrode and covering window; the sweep rate must be low (less than 5 mV s^{-1} is necessary), because of the diffusion characteristics of the thin film electrolyte layer in the cell [9] and resolution of collected IR spectra (4 cm^{-1} or better). The length of the potential step applied during the scanning of an IR-spectra is dependent on the sweep rate, the resolution of the spectra and the number of collected interferograms. The potentiostatic and galvanostatic measurements must be carried out with the working electrode at a large distance ($> 200 \text{ }\mu\text{m}$, [9]) away from the infrared transparent window to secure an undisturbed progress of electrochemical processes on the electrode surface. High absorption of the thick layer of the electrolyte dictates that the measurement of an IR-spectrum at the potential of interest must be accomplished in a thin layer arrangement. Thus, the electrode must be moved to an optimal and reproducible distance to the window. Any change of the electrode potential due to deviation of the geometry from an undisturbed electrochemical system to a thin layer arrangement could be overcome by switching from the galvanostatic to the potentiostatic mode of measurement during the collection of an IR spectra.

Experimental

Preparation of Li/Co-Oxide Thin Films

Alcoholic Li/Co-sols were prepared from Co(II)-acetate ($(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$, Aldrich) and Li(I)-acetate ($\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, Aldrich) precursors. A mixture of Co(II)-acetate and Li(I)-acetate (molar ratio $x = n(\text{Co}^{2+})/n(\text{Li}^+) = 1$) was dissolved with the slow addition of an aqueous solution (30 vol.%) of H_2O_2 (Fluka), which caused a highly exothermic reaction. The control of the reaction was accomplished by cooling the mixture with tap water. After completion of the reaction and addition of excess of the H_2O_2 , the resulting solutions were freeze-dried in vacuum. Freeze-dried precipitates were dissolved in alcohol ($V \approx 100$ ml, 95% ethanol or methanol) to get brown Li/Co-sols which were appropriate for the deposition of films by a dip-coating technique. Sols remained stable in the refrigerator ($T \approx +5$ °C) for up to few months. Additional heating of alcoholic sols at 60 °C for short times (few hours) led to gelation into optically transparent gels. Heat treatment of dry xerogel powders or thin films at different temperatures gives Li/Co-oxide films and powders exhibiting various stoichiometries and structural phases.

Thin Film Deposition

Li/Co-oxide films were deposited by the dip-coating technique either on glass plates coated by the ITO ($\text{In}_2\text{O}_3 : \text{Sn}$), FTO ($\text{SnO}_2 : \text{F}$) electrically conductive thin film ($R_s \approx 10 \Omega/\square$) (Pilkington, UK) or on different metallic substrates (Al, Pt, stainless steel). The substrates were cleaned with chrome-sulfuric acid, rinsed with deionized water and dried at 60 °C. The metallic substrates were also cleaned by surfactants, organic solvents and water. Deposition of films was made by using a purpose-built motor-driven dip-coating unit with a pulling rate of the substrate in the range between 1 and 10 cm min^{-1} . Dry Li/Co-xerogel films were heat-treated at 500 °C for 1 hour in air. The thickness of the oxide films produced by a single dipping cycle was from 60 to 250 nm depending on the viscosity of the sols (not measured).

Other Measurements Techniques and Equipment

Crystal structures of Li/Co-oxide films were derived by X-ray diffraction (XRD) analysis, using a Philips PW 1710 X-ray Diffractometer. CuK_α radiation was used and the diffraction data points were recorded every 0.02° of 2θ .

The average oxidation state of Co was determined by adding 10 ml of 0.01 M Fe(II) ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$ -Mohr's salt, Fluka), 10 ml of 96% H_2SO_4 (Fluka) and 10 ml of 85% H_3PO_4 (Fluka) to 2-5 mg of oxide film while passing

an Ar stream through the bottle with the mixture. The solution was back titrated with a standard solution of 0.01 M $K_2Cr_2O_7$ (Aldrich), using diphenylamine as indicator. The total Co content was determined by titration with 0.1 M EDTA (Sigma) after dissolution of similar amounts of sample in concentrated HCl and neutralization with $(NH_3)_{aq}$. The Li/Co ratios were determined by atomic emission spectroscopy (ICP-AES) on a Thermo Jarrel Ash ICP-AES Atom Scan 25 analyzer.

The thickness of thin films was measured on a Surface Profiler Alfa Step 2000 with the maximum resolution of 5 nm.

The potentiodynamic (cyclic voltammetry) measurements were performed with an EG&G PAR model 273 computer-controlled potentiostat-galvanostat, driven by the model 270 Electrochemical Analysis software. A three-electrode system with 1 M $LiSO_3CF_3$ in PC electrolyte was used for the electrochemical measurements. The electrolyte was purged with pure argon (99.99 %, oxygen free) for 15 minutes prior to analysis. All potentials were measured against the modified Ag/AgCl reference electrode ($E_0 = +0.212$ V vs. SHE). The structure, stoichiometry and the thickness of the Li/Co-oxide film on the Pt working electrode were determined before the spectroelectrochemical investigation by the methods described above. The working electrode was positioned in a Teflon holder of the cell in a thin layer ($\approx 5 \mu m$) arrangement for potentiodynamic measurements, which were carried in a potential range between +1.40 V and -1.00 V applying sweep rates around 1 mV s^{-1} when using a thin layer arrangement.

FT-IR spectra were recorded on a Perkin Elmer System 2000 FT-IR spectrophotometer with a resolution of 4 cm^{-1} in the spectral range between 4000 and 400 cm^{-1} . For each spectrum 30 interferograms were sampled. The reference spectrum was obtained at the open circuit potential (E_{opc}) of the cell.

Results and Discussion

XRD Characterization of as Deposited Li/Co Thin Film on Pt Substrate

XRD pattern of an as deposited Li/Co oxide film on Pt substrate ($d_f = 270 \text{ nm}$) is presented in Figure 5. The diffraction peaks were characteristic of layered Li_xCoO_2 ($0 < x < 1$) rhombohedral ($R\bar{3}m$) structure. Determination of stoichiometry showed the presence of small excess of Co^{2+} ions and deficit of Li^+ ions in the film structure. A stoichiometric formula of $Li_{0.99}Co_{1.01}O_2$ was determined for the as deposited oxide film.

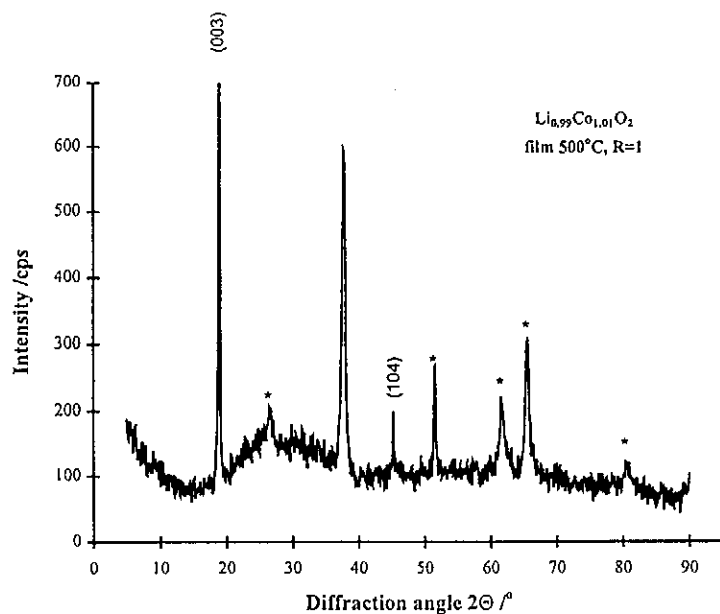


Fig. 5 XRD pattern of as deposit layered $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ rhombohedral $\bar{R}3m$ oxide film on Pt substrate (500 °C, 1h, $d_f = 270$ nm). * — diffraction lines of FTO/glass substrate

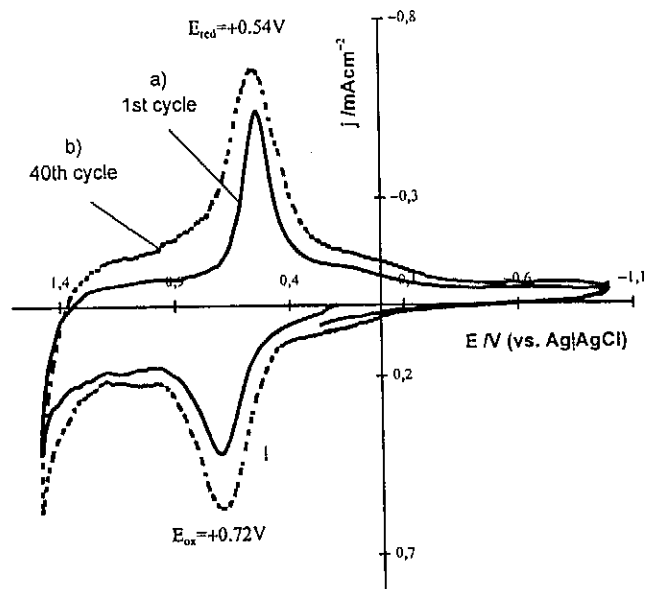
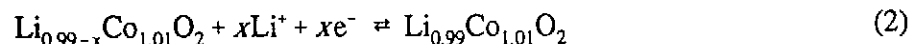


Fig. 6 Cyclic voltammogram of the $\text{Li}_x\text{Co}_{1.01}\text{O}_2$ ($0.5 \leq x \leq 0.99$) thin film electrode at 1 mV s^{-1} in propylene carbonate containing $1 \text{ mol l}^{-1} \text{ LiSO}_3\text{CF}_3$. (a) 1st cycle. (b) 40th cycle

The *in-situ* spectroelectrochemical measurements under potentiodynamic conditions were carried out with the $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2/\text{Pt}$ working electrode between an anodic potential limit of +1.40 V, where the decomposition of the electrolyte was observed, and a cathodic potential -1.00 V, where almost no current response was detected.

The first cycle of a cyclovoltammogram obtained with a sweep rate of 1 mV s^{-1} (Fig. 6a) was started in positive potential direction at the open circuit potential $E_{opc} \approx +0.20 \text{ V}$. The appearance of an oxidation current with a peak potential $E_{ox} \approx +0.72 \text{ V}$ was connected with deintercalation of Li^+ ions out of the $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ oxide film structure, accompanied by simultaneous oxidation of a corresponding amount of Co^{3+} ions in the crystal lattice to the Co^{4+} oxidation state. Deintercalation of Li^+ ions out of the $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ oxide film structure was accompanied by a coloring of the film to dark gray-brown color. In the negative potential sweep, a reduction current peak was observed at $E_{red} \approx +0.54 \text{ V}$ which was assigned to intercalation of Li^+ ions into the $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ structure and simultaneous reduction of Co^{4+} ions back to the Co(III) oxidation state. At the intercalation process the color of the film changed into the native yellow state. The intercalation/deintercalation process is described by the Eq. (2)



Oxidation and reduction peaks were increased in subsequent cycles (Fig. 6b), which showed that the structure of the film was becoming less rigid. This enables Li^+ ions to move more easily and in greater amount in and out of the film structure. Constant intercalation/deintercalation and electrochromic response was achieved after about 60 cycles. Similar behavior was observed also for powder samples of layered rhombohedral Li_xCoO_2 ($x \approx 1$) and Li_xNiO_2 ($x \approx 1$) oxides, prepared by solid state reactions, which were investigated in "rocking chair" batteries [15].

The reference infrared spectrum (Fig. 7) was recorded at the open circuit potential $E_{opc} \approx +0.20 \text{ V}$ of the as deposited $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ oxide film on Pt substrate which was put into *in-situ* spectroelectrochemical cell filled with 1 M $\text{LiSO}_3\text{CF}_3/\text{PC}$ electrolyte. The working electrode was positioned at about $5 \mu\text{m}$ from the covering silicon window. The reference spectrum showed a number of vibrational bands which were indicative of PC and triflate (LiSO_3CF_3), containing various C=O, C-O, O-Li and C-H modes. The appearance of a broad vibrational band between 3000 and 3600 cm^{-1} , characteristic of stretching vibrations of H_2O , showed that the electrolyte also contained some moisture, because the measurements and the preparation of the cell were not performed in dry atmosphere.

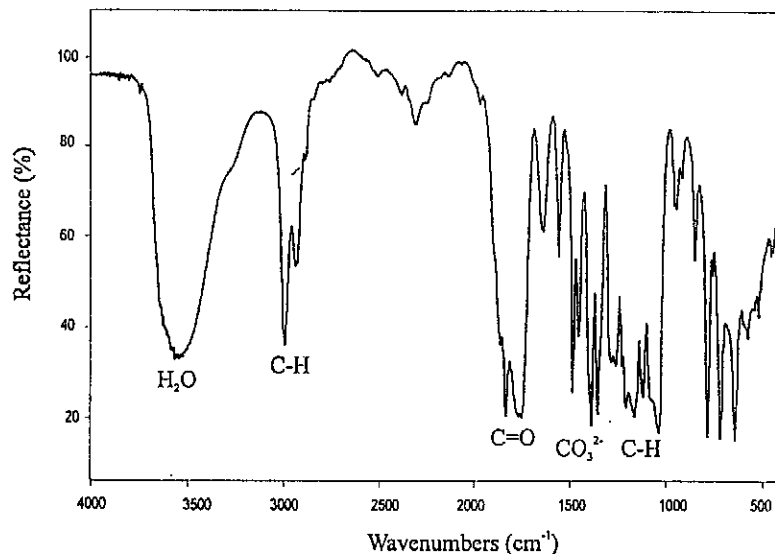


Fig. 7 The reference reflection-absorption FT-IR spectrum ($\Phi_B \approx 73^\circ$) obtained at open circuit potential $E_{opc} \approx +0.20$ V of the as deposited $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ oxide film on Pt substrate which was put into in-situ spectroelectrochemical cell filled with 1 M $\text{LiSO}_3\text{CF}_3/\text{PC}$ electrolyte

The subsequent spectrum recorded at +0.40 V and also reflection-absorption FT-IR spectra obtained at other potentials were very much alike to each other. To get rid of the redundant absorption of the electrolyte, which blurred out the fine differences in the spectra, the SNIFTIR technique was used.

In Fig. 8a, b the subtracted normalized spectra according to the method described before are shown. Normalized reflectance spectra obtained at different potentials during deintercalation of Li^+ ions out of the $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ oxide film structure (Fig. 8a) showed that at around +0.6 V, a negative vibrational band started to appear at the frequency of 684 cm^{-1} . The appearance of this band was caused by the decrease in the absorption of longitudinal optical mode (LO), which corresponds to the crystal lattice vibration of the CoO_6 octaheder in the structure of the film. The intensity of this phonon band was increased up to +1.0 V, whereupon it started to decrease. Closer inspection of the band showed a red shift of the LO frequency to 674 cm^{-1} at more positive potentials ($E \approx +1.0$ V). The appearance of this band and of its red shift to lower frequencies could be explained by structural and electronic changes which are taking place during the deintercalation process. The extraction of Li^+ ions and electrons out of the film structure causes a weakening of the O-Co-O bond between cobalt and oxygen ions in the CoO_6 octaheder and a change in the oxidation state of some amount of Co^{3+} ions to the oxidation state of +4. Changes in the electronic structure of the film cause the appearance of polarons which are connected with

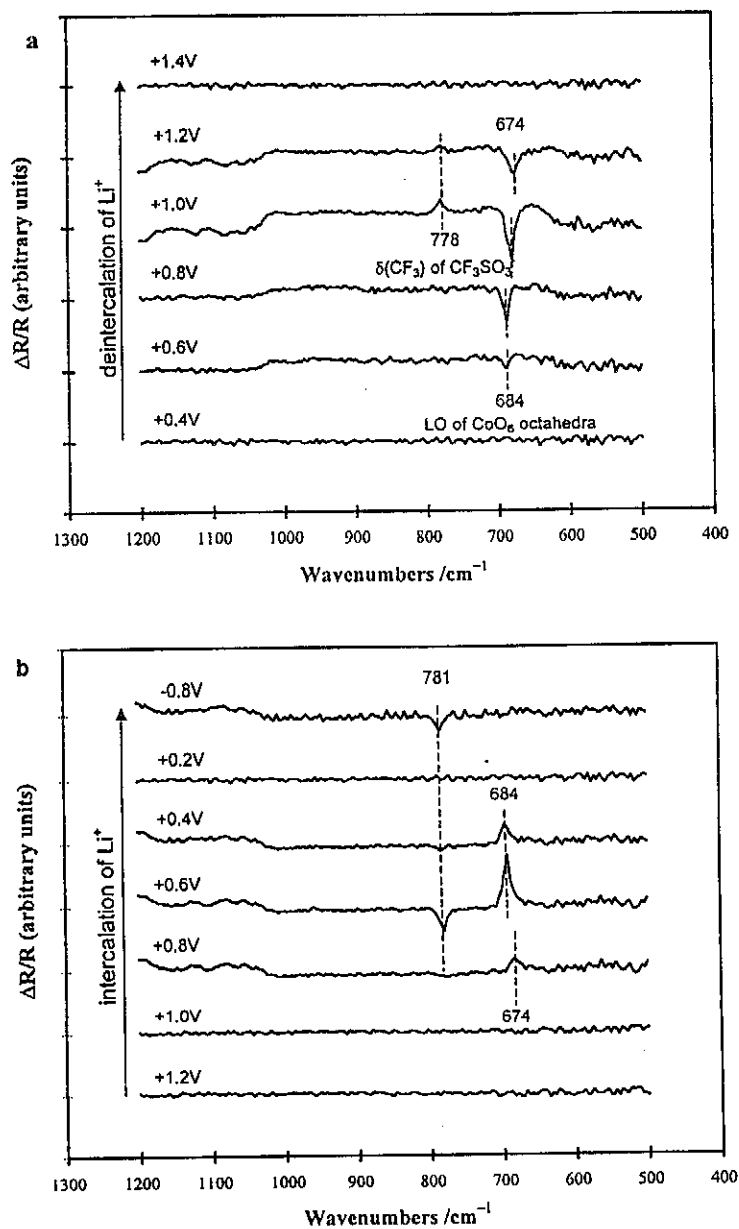


Fig. 8 Subtracted normalized FT-IR (SNIFTIR) spectra: (a) obtained at different potentials at deintercalation of Li⁺ ions out of the Li_xCo_{1.01}O₂ (0.5 ≤ x ≤ 0.99) oxide film structure, (b) obtained at different potentials at intercalation of Li⁺ ions into the Li_xCo_{1.01}O₂ (0.5 ≤ x ≤ 0.99) oxide film structure. The spectra are presented in the spectral region between 1200 and 500 cm⁻¹

the coloring of the film. The coupling of polaron and phonon could lead to the decreased absorption in the reflection-absorption spectra and to the red shift of the LO frequency during deintercalation of Li^+ ions. Generation of holes during the deintercalation process increases the electric conductivity of the LiCoO_2 film, which is a p -type semiconductor [16]. The film then starts to behave more like a metal substrate, and the result is a decrease of absorption or an increase of reflection of IR radiation at the surface of the film.

Close inspection of the LO phonon band presented in Fig. 9 shows a splitting of this band into two, which indicates a decrease in the symmetry of the crystal lattice and a possible phase transformation.

Another very interesting feature in Fig. 8a is the appearance of a positive vibrational band at 778 cm^{-1} , which corresponds to the symmetrical bending vibration $\delta(\text{CF}_3)$ of CF_3 (trifluoromethyl) groups of the triflate ion (CF_3SO_3^-). This vibrational band appears at highly positive potentials where the majority of Li^+ is already deintercalated and remains close to the surface of the film. The excess of positive charge on the electrode is compensated by the rearrangement of triflate ions making the vibrating dipole of the CF_3 group oriented more or less perpendicularly to the surface of the electrode.

During the intercalation process (Fig. 8b), restoration of the intensity and a blue shift of the frequency to the initial value (684 cm^{-1}) of the LO phonon

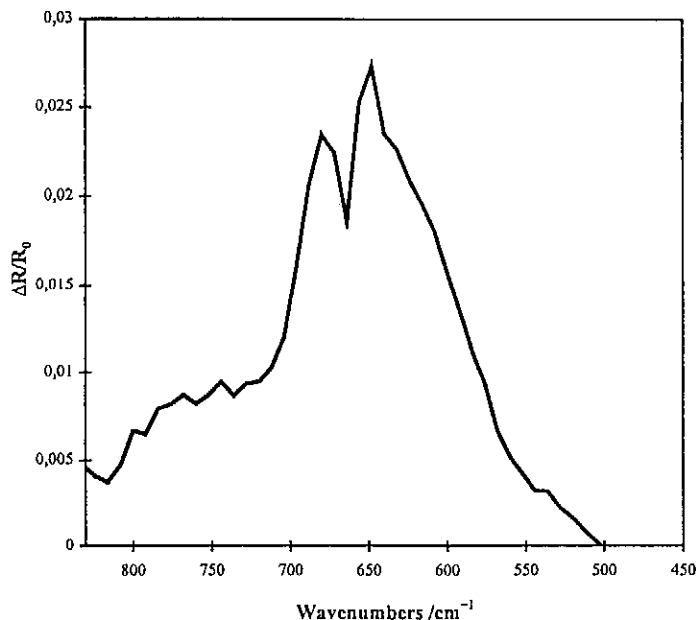


Fig. 9 Subtracted normalized FT-IR (SNIFTIR) spectrum of $\text{Li}_x\text{Co}_{1.01}\text{O}_2$ ($0.5 \leq x \leq 0.99$) oxide film obtained at deintercalation process ($E \approx +1.0 \text{ V}$) presented in the spectral region between 900 and 400 cm^{-1}

band is observed. These effects indicate a reversible nature of the structural and electronic changes during the deintercalation/intercalation processes.

A further interesting feature appears at more negative potentials of the electrode where a negative band for the vibration of CF_3 group of triflate ions appears. This can be explained by a new rearrangement of triflate ions due to the negative potential of the electrode. The ions must have turned around by about 180° to be again in the position where resonance absorption in the IR spectra can be observed.

Conclusion

In this study external reflection FT-IR spectroscopy was demonstrated to be a very useful tool which can be efficiently used for the elucidation of electrode processes. *In-situ* FT-IR spectroelectrochemical measurements allow direct monitoring of the electrode processes without removing the electrode from the electrochemical environment. The design of the FT-IR spectroelectrochemical cell enables a simple and accurate adjustment of the working electrode in the cell. The SNIFTIR method facilitates detection of small differences appearing in the reflection-absorption spectra obtained at different potentials.

Investigations of $\text{Li}_{0.99}\text{Co}_{1.01}\text{O}_2$ oxide thin film deposited on Pt substrate under potentiodynamic conditions show that during deintercalation/intercalation processes of Li^+ ions, reversible structural and electronic changes in the electrode material appear. These changes are accompanied by the structural rearrangement of the electrolyte at the electrode/electrolyte interface.

Last but not least, the equipment for such kind of measurements is accessible with some skill to every laboratory.

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