Adsorption of ethylene carbonate on lithium cobalt oxide thin films: A synchrotron-based spectroscopic study of the surface chemistry

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A B S T R A C T

The surface chemistry of cathodic lithium cobalt oxide ($LiCoO_2$) in contact with the Li-ion battery solvent ethylene carbonate (EC) was studied *via* synchrotron based soft X-ray photoelectron spectroscopy (SXPS). By stepwise in-situ adsorption of EC onto an rf-magnetron sputtered $LiCoO_2$ thin film and consecutive recording of SXPS spectra, the chemical and electronic properties of the interface were determined. EC partially decomposes and forms a predominantly organic adlayer. Prolonged exposure results in the formation of a condensed EC layer, demonstrating that the decomposition layer has passivating properties. Lithium ions deintercalate from the electrode and are dissolved in the adsorbate phase, without forming a large amount of Li-containing reaction products, indicating that electrolyte reduction remains limited. Due to a large offset between the $LiCoO_2$ valence band and the EC HOMO, oxidation of EC molecules is unlikely, and should require energy level shifts due to interaction or double layer effects for real systems.

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1. Introduction

The efficiency of ion transfer at the interfaces between the electrode and the electrolyte is crucial for the performance of Li-ion intercalation batteries [1]. Processes known to occur at intercalation cathodes are electrolyte oxidation, chemical reactions and decomposition of electrolyte species like solvent molecules [2]. These side reactions contribute to the formation of the solid electrolyte interface layer (SEI), consisting of inorganic and organic compounds, which determines not only the lifetime of accumulator batteries, but also consists of chemical phases which alter the electrochemical behavior of the cathode material [3].

A surface science experiment can provide experimental data on the electron level alignment, surface chemistry and fundamental charge-transfer processes at the electrode-electrolyte interface [4]. This has been demonstrated using molecular probes [5,6] and for solvent molecules used in liquid electrolytes like DEC (dimethy carbonate) [7,8], DMSO (dimethyl sulfoxide) [9], and for water [2,10], as well as for solid thin film electrolytes like lithium phosphorus oxynitride (LiPON) glass [11–14]. Solid-solid interfaces are also present in all liquid-based concepts in the form of SEI interfaces, and are highly relevant for future particle-based solid-state batteries. With the help of experimental data, strategies to improve the critical interfaces can be developed [2,4,15], e.g. using passivat-

ing coatings [16]. Nevertheless, interface experiments are scarcely used to investigate the complex layer systems of intercalation batteries based on surface science experiments, often due to the electronically insolating nature of the electrolyte and the need for sophisticated preparation steps in ultrahigh vacuum (UHV). But only with reliable data from various interfaces, conclusions about general mechanisms and processes can be drawn and correlations can be found.

In general, as schematically drawn in Fig. 1, adsorbing solvent molecules can form a weakly bond phase, often with van-der-Waals forces dominating the interface (physisorption). Secondly, they can chemically react, forming new strong chemical bonds (chemisorption) and new electronic states, e.g. gap states. Alternatively, the molecules can dissociate, when intramolecular bonds break or realign and decomposed species stick to the surface as reaction products. Moreover, even integer charges can be transferred and lithium ions can move into a molecular layer [23] or accumulate in a solvated state at the interface [4]. Additionally, the redistribution of charges or a specific orientation of adjacent species with a molecular dipole can lead to interface dipole formation [19,24]. Since transition metal oxides exhibit semiconducting behavior, they fall subject to band bending. Especially important for transition metal oxides is the question, whether the discussed phenomena lead to further oxidation or reduction of the cathodic layer. As state-of-the-art material and model system, often $LiCoO_2$ thin films are chosen for related experiments.
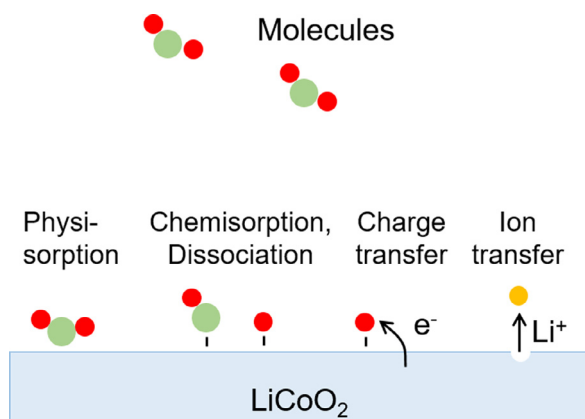
Fig. 1. Possible processes for molecule adsorption and interphase formation on a LiCoO$_2$ thin film.

The structure of the (00l) surface of LiCoO$_2$ [11] and its implications for photoelectron spectra have been discussed in [6,17,18]. Calculations indicate that termination occurs by the oxygen layer partially covered with lithium [18]. This is in agreement with the surface components observed in photoelectron spectra, although surface species such as lithium hydroxide cannot be fully excluded. Additionally, intercalation materials such as LiCoO$_2$ contain mobile lithium, which is free to participate in the formation of surface layers.

Here, an in-situ adsorption experiment of C$_3$H$_4$O$_3$ ethylene carbonate (EC), a common solvent for liquid electrolytes, on an rf-magnetron sputtered, (00l) textured LiCoO$_2$ thin film is presented. The core level and the valence band were probed to identify the chemical reactions, deduce fundamental charge-transfer processes and to comment on the energy level alignment at the interface. As excitation source for X-ray photoelectron spectroscopy, synchrotron radiation was used (SXPS), to investigate the complex chemical reactions on interface formation in detail, especially benefiting from a superior cross-section in the Li1s core level region.

2. Experimental

2.1. SXPS

All experiments were carried out at the undulator beamline U49/2 of BESSY II at Helmholtz-Zentrum Berlin, using the SoLiAS (S̲olid/L̲iquid A̲nalysis S̲ystem) multi-chamber UHV-system. The adsorption chamber with a base pressure of $5 \cdot 10^{-10}$ mbar is connected directly to the analysis chamber equipped with a hemispherical analyzer (Phoibos 150, SPECS). All spectra were background subtracted using the Shirley method [19]. Intensities were normalized to the electron storage ring current. For calibration of the energy scale, a sputter-cleaned gold sample was used. After the first adsorption step, the binding energy scale of the C1s spectra was referenced to the C—C peak (adventitious carbon) at 284.7 eV. The Co2p, O1s, Li1s and valence band spectra were normalized to the respective substrates main peak, due to instrumental shifts of the binding energy scale during the interface experiment. For all recorded spectra, a kinetic energy excess of 120 eV was chosen. Therefore, the excitation energy E$_{exc}$ was varied as stated. To avoid possible beam damage, recording time for the spectra was optimized and a high cff-factor was chosen to reduce the photon flux. To estimate possible beam damage, the C1s core level spectrum was recorded for each adsorption step at the beginning of the measurement as well as at the very end. We identified only minor beam damage, and therefore only negligible

variations in the C1s and O1s signal of the respective components. Additionally, results were double-checked by changing the measurement spot on the sample.

2.2. LiCoO$_2$

The LiCoO$_2$ substrate was radio frequency (rf) magnetron sputtered in an argon/oxygen atmosphere (6 SCCM Ar, 6 SCCM O$_2$) at a working pressure of $8 \cdot 10^{-3}$ mbar on *n*-doped Si(1 1 1) wafer plates. To obtain the high temperature (HT) LiCoO$_2$ phase, the film was deposited at a temperature of 550 °C. The quality of the thin film was analyzed *via* SXPS and stoichiometric LiCoO$_2$ was found [20].

2.3. Adsorption experiment

The liquid adsorbents were stored and handled under an argon atmosphere and exposed to a molecular sieve before filling into a Schlenk-type glass flask connected to a separated adsorption chamber. Vacuum distillation was used to purify the solvent. The dosage was controlled by a leak valve and the exposure time was varied stepwise to match the desired dosage (from 0.5 Langmuir (L) to 4 L), after each adsorption step the sample was transferred to the analysis chamber to perform SXPS. From the attenuation of the substrate core levels we conclude, that the coverage of the LiCoO$_2$ was still in the range of one Monolayer after 4 L EC.

2.4. Spectra interpretation

The peaks were fitted using a pseudo-Voigt function

$$f(E) = y_0 + A\left[m_u \frac{2}{\pi} \frac{w_L}{4(x-x_c)^2 + w_L^2} + (1-m_u)\frac{\sqrt{4ln2}}{\sqrt{\pi}w_G} e^{-\frac{4ln2}{w_G}(x-x_c)^2}\right]$$

were w_L is the FWHM of the Lorentzian function, w_G is the FWHM of the Gaussian function, and m_u is the ratio between the Lorentzian and Gaussian distributions. For the ratio, a constant factor $m_u = 0.2$ was chosen, the Gaussian FWHM was set to $w_G = 1.4$ eV and the Lorentzian FWHM was varied with the binding energy of the experimentally probed energy levels, $w_L = 1.4$ for the C1s region and $w_L = 1.5$ eV for the O1s region.

3. Results and discussion

Fig. 2 shows the detailed SXPS spectra of the relevant core level regions of the interface between LiCoO$_2$ and EC, consecutively recorded after each adsorption step. The Co2p$_{3/2}$ main emission has a binding energy of 778.0 eV, as commonly observed for Co^{3+} in LiCoO$_2$ [21]. The oxidation state of the cobalt is correlated to respective satellite structures of the Co2p$_{3/2}$ peak due to final state effects, representing the Co^{3+} ($\Delta E = 10$ eV) and Co^{2+} (S2, $\Delta E = 6$ eV) oxidation state. For a fully lithiated cathode, the oxidation state is purely Co^{3+} in an ideal case. If a reduction of the cathode material occurs, the intensity of the S2 satellite will increase, while the main emission peak will show a slight shoulder at higher binding energies, due to a 1.1 eV higher binding energy of the Co^{2+} species compared to the Co^{3+} main emission. However, during the interface experiment, no change of the oxidation state could be detected in the satellite region S2 of the Co2p$_{3/2}$ spectrum.

While the Co core level is unique to the substrate phase, the O1s region in Fig. 2 exhibits new features between 531 eV and 536 eV with increasing EC dosage, which can be assigned to the adsorption phase. Corresponding features in the C1s region start to evolve for 1 L EC dosage and are unique to the adlayer. In the following, the O1s and C1s spectra will be firstly discussed in detail in terms of the chemical reactivity and adlayer formation of the EC molecules.