Monitoring electrode/electrolyte interfaces of Li-ion batteries under working conditions: A surface-enhanced Raman spectroscopic study on LiCoO$_2$ composite cathodes

Marcel Heber and Christian Hess*

Eduard-Zintl-Institute of Inorganic and Physical Chemistry, Technical University of Darmstadt, Alarich-Weiss-Str. 8, 64287 Darmstadt, Germany

*E-mail: christian.hess@tu-darmstadt.de
Abstract

Lithium-ion batteries are commonly used for electrical energy storage in portable devices and are promising systems for large-scale energy storage. However, their application is still limited due to electrode degradation and stability issues. To enhance the fundamental understanding of electrode degradation we report on the Raman spectroscopic characterization of LiCoO$_2$ cathode materials of working Li-ion batteries. To facilitate the spectroscopic analysis of the SEI (solid electrolyte interface) we apply surface-enhanced Raman spectroscopy by using Au nanoparticles coated with a thin SiO$_2$ layer (Au@SiO$_2$). We observe a surface-enhanced Raman signal of Li$_2$CO$_3$ at 1090 cm$^{-1}$ during electrochemical cycling as an intermediate. Its formation/decomposition highlights the role of Li$_2$CO$_3$ as a component of the SEI on LiCoO$_2$ composite cathodes. Our results demonstrate the potential of Raman spectroscopy to monitor electrode/electrolyte interfaces of lithium-ion batteries under working conditions thus allowing relations between electrochemical performance and structural changes to be established.

Keywords: lithium batteries, solid electrolyte interface, LiCoO$_2$, in situ spectroscopy, Raman spectroscopy, SERS, SHINERS
1. Introduction

In light of the climate change and scarcity of fossil fuels, the topic of sustainable energy production and their usage becomes more and more relevant. In addition to the use of renewable energy sources, the storage of energy and the conversion of the transportation industry to electric vehicles represent important challenges for today's research, in which batteries play a key role. Among the rechargeable batteries, especially the lithium-ion battery is used in electronic devices [1]. The commercial lithium-ion battery contains e.g. LiCoO$_2$ as cathode material. Advantages of LiCoO$_2$ are its high specific capacity, low self-discharge, and high cycle life [2]. During the initial charging and discharging processes of the lithium-ion battery, a coating layer (SEI = solid electrolyte interface) forms on the electrode surface due to the reaction between the electrolyte and the cathode material, which may influence the capacity and life time of the battery [1,3]. A detailed characterization of the composition and formation processes of the top layer is therefore essential for the efficient use of lithium-ion batteries [4,5]. This layer is permeable to lithium ions and causes passivation of the electrode material [1], protecting it against further surface reactions and dendrite formation [6]. However, due to the formation of the SEI, some of the lithium ions are irreversibly lost. Furthermore, it represents an additional diffusion resistance, which can be speed-determining depending on the ion conductivity of the formed layer [7]. Reports on the chemical composition of the SEI include inorganic compounds such as Li$_2$O, LiF, and Li$_2$CO$_3$ [5,6], and organic compounds such as ROCO$_2$Li, ROLi, and LiOH [5,8-12]. There are several ex situ but only few in situ techniques available to study the electrode-electrolyte interface [5], such as XRR (X-ray reflectometry), NR (neutron reflectometry), and SERS (surface-enhanced Raman spectroscopy) [5,9,12]. For the characterization of the electrode material, Raman spectroscopy has proved to be a powerful method, as it can be performed without specific sample preparation and is suitable for
in situ measurements [5,13], thus allowing to monitor the dynamics inside the active material during the electrochemical process and to establish relations between electrochemical performance and structural changes. The literature describes a high temperature (HT) and a low temperature (LT) phase of LiCoO$_2$. In this study, HT-LiCoO$_2$ is used as a cathode material, which crystallizes in a hexagonal layer structure (space group R$\bar{3}$m) [14], consisting of a close-packed network of oxygen atoms with the Li$^+$ and Co$^{3+}$ ions ordering on alternating (111) planes of the cubic rock-salt structure [15]. According to its space group, the irreducible representation is $A_{1g}+2A_{2u}+E_g+2E_u$, and the odd vibrational modes are Raman-inactive, while the straight modes are Raman active ($A_{1g}$ and $E_g$) [13]. The first Raman study on LiCoO$_2$ was reported by Inaba et al. [16], in which the effect of the lithium content on the Raman-active bands was investigated, showing a reduction of the signal intensity due to deintercalation [16]. A disadvantage of normal Raman spectroscopy is its low sensitivity, which makes detection of the SEI layer difficult [17]. However, this issue can be resolved by using SERS [18], which provides a signal enhancement of up to six orders of magnitude [19] near rough Au, Ag or Cu surfaces [17], and has enabled identification of chemical species and detailed structural characterization in various research fields, including materials science, biosensing, catalysis, and electrochemistry [20]. Electrochemical electrodes are typically metal surfaces, allowing the direct application of SERS to study the behavior of adsorbed molecules [20-24], such as tetrathiafulvalene (TTF) derivatives extensively used in mechanostereochemistry and molecular electronic devices [20-22]. Using SHINERS, the SERS effect can be transferred to any sample surface, by coating metal nanoparticles with an inert shell such as SiO$_2$ or Al$_2$O$_3$ [25]. Hy et al. applied this approach to surface reactions on lithium-rich cathode materials (Li[Ni$_x$Li$_{(1-2x)/3}$Mn$_{(2-x)/3}$]O$_2$, $0 \leq x \leq 0.5$) during electrochemical cycling, and reported on the detection of intermediately formed Li$_2$O, leading to
Li$_2$CO$_3$ as a result of decomposition reactions of the electrolyte at the cathode [26]. Teshager et al. examined lithium-rich Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ (LLNMO) and LiCoO$_2$ cathodes during first- and second-cycle charging and discharging with diffuse reflectance infrared Fourier-transformed spectroscopy (DRIFTS) while circulating the electrolyte [27]. This raises the question whether the conditions under electrolyte circulation can be compared to those of a conventional battery under working conditions. The authors reported various SEI species, e.g., RCOOR, Li$_2$CO$_3$, and RCO$\text{Li}$, during charging above 4.0 and 4.5V and during discharging below 3.6 and 4.0 V for LiCoO$_2$ and LLNMO, respectively, attributed to EC decomposition [27]. In the context of Li-ion and Li-O$_2$ cells, Galloway et al. observed the formation of LiO$_2$, Li$_2$O$_2$, and Li$_2$CO$_3$ on lithium metal and planar carbon electrode interfaces, as well as on composite carbon black electrodes [28].

In this study, we use surface-enhanced Raman spectroscopy to study LiCoO$_2$ composite cathodes during electrochemical cycling. First, the synthesis and characterization of the shell-isolated Au@SiO$_2$ nanoparticles is presented. We then apply the nanoparticles to LiCoO$_2$ composite cathodes, allowing us to identify chemical species of the SEI layer and to monitor their dynamic behavior during electrochemical cycling.

### 2. Experimental section

#### 2.1 Synthesis of the composite cathode

The synthesis of LiCoO$_2$ follows the Pechini process, which ensures a statistical distribution of the cations in the material [29]. LiNO$_3$ (Merck KGaA, ≥ 98 %), Co(NO$_3$)$_2$$\times$6H$_2$O (Merck KGaA, ≥ 99.0 %), and citric acid (AppliChem, ≥ 98%) are weighted and dissolved in water. A concentrated ammonia solution (25 %) is then added dropwise to the solution until the pH value is adjusted to
5. Ethylene glycol is added into the suspension and the temperature is set to 180 °C for six hours. The resulting black solid is first collected and ground, and then pre-calcined at 450 °C for six hours (heating rate: 1.5 °C/min). The obtained brown powder is ground and calcined at 800 °C for 25 hours (heating rate: 20 °C/min).

For the preparation of the composite cathode, the obtained LiCoO$_2$ is mixed with carbon black (TIMCAL, super p) and PVDF (Polyvinylidenfluorid, Solef, 6020/1001 H-6091) with a weight ratio of 84:8:8. By adding N-methyl-2-pyrrolidone (NMP) dropwise into the mixture, a thick flowing slurry is formed, which is then brushed on an aluminum net and dried overnight. The final material is cut into 12 mm round plates for insertion into the test cell.

2.2. Synthesis of Au@SiO$_2$

An aqueous solution of gold chloric acid (HAuCl$_4$·3H$_2$O, Sigma-Aldrich, ≥ 99.9%) is refluxed in a three-necked flask. To the boiling solution 3% TSC (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, Sigma Aldrich, ≥ 99.9%) solution is added, and stirred for further 15 min under reflux. Then the solution is cooled to room temperature. PVP (Polyvinylpyrrolidon, Sigma Aldrich, MW = 40,000 g mol$^{-1}$) solution at a concentration of 12.8 mg/mL is added and stirred at room temperature overnight. After centrifuging, the sample is dispersed in water. The AuNP (gold nanoparticles) solution is added rapidly to a solution of anhydrous ethanol (Sigma-Aldrich, ≥ 99.8%), water, and 25 wt% NH$_4$OH solution.

For the preparation of coated gold nanoparticles (Au@SiO$_2$), 2.5 to 50 μl TEOS (Tetraethyl orthosilicate, Sigma Aldrich, ≥ 98%) in anhydrous ethanol is added to the solution. The solution is stirred for four hours at room temperature and then centrifuged. The residue is washed three
times with anhydrous ethanol. After each washing step, the solution is centrifuged again. The residue is dispersed in water.

### 2.3 Characterization of Au@SiO$_2$

The coated nanoparticles were checked for conformity by the gold catalyzed reduction of p-nitrophenol as an integral probe [30]. To this end, water, NaBH$_4$-solution (Merck), and 0.01 M p-nitrophenol are mixed in a cuvette. To this mixture, 100 µl of the nanoparticle solution is added and monitored by UV-VIS spectroscopy (Jasco V-770).

### 2.4 Raman spectroscopy

Raman experiments were performed by using 632 nm laser excitation from a diode laser (Ondax). The scattered light was sent to a transmission spectrometer (Kaiser Optical, HL5R) equipped with an electrically cooled CCD detector with 256×1024 pixels. The elastically scattered light was blocked by SuperNotch Plus filters (Kaiser Optical). For calibration of the spectrometer emission lines of standard Ne lamp were used. The spectral resolution was 5 cm$^{-1}$; the wavelength stability was better than 0.5 cm$^{-1}$. The laser power was set to 3.8 mW as measured at the position of the sample with a power meter (Ophir). The acquisition time for a single spectrum was 240 s, including the application of a cosmic ray filter and subtraction of the dark spectrum (laser off).

*In situ* Raman experiments were performed in a 180° backscattering geometry using a commercial test cell (EL Cell) [30] equipped with a glass optical window (see Figure 1). The battery cell consists of two electrodes separated by a layer of glass fiber filter paper soaked with electrolyte to prevent a short circuit.
Figure 1. Left: In situ Raman spectroscopic analysis (632 nm) in the presence of Au@SiO$_2$ particles. Right: CV curve for the first cycle of the LiCoO$_2$ composite cathode. Metallic Li served as counter electrode and LP30 as electrolyte. Red points indicate the starting time of Raman measurements during cycling.

Cyclovoltammetric (CV) cycling was performed using a potentiostat from BioLogic (VSP). Metallic Li served as counter electrode at a cycling rate of 0.3 mV/s using potential limits of $E_{\text{min}} = 3.2$ V and $E_{\text{max}} = 4.2$ V. The electrolyte LP30 (Sigma-Aldrich, battery grade, impurities: < 50 ppm in HF, < 15 ppm H$_2$O) consisted of 1M LiPF$_6$ dissolved in ethylene carbonate and dimethyl carbonate (ratio 1:1). Raman spectra under quasi in situ conditions were recorded after six cycles. In situ Raman spectra were recorded continuously every four minutes during electrochemical cycling, as indicated in Figure 1. The CV profile of the in situ experiment is shown in the supporting information (see Figure S1). The test cell used for all Raman experiments made no observable contribution to the Raman signal. As part of the data analysis a least-square fit analysis was performed by using Voigt functions.
3. Results and discussion

For the analysis of the electrode/electrolyte interface we employ gold nanoparticles coated with SiO$_2$ (Au@SiO$_2$). Based on TEM images the gold nanoparticles possess an average diameter of 53 nm, whereas the thickness of the SiO$_2$ layer ranges between 5 and 34 nm (average: 29 nm). A TEM image of Au@SiO$_2$ nanoparticles employed in this study is shown in the left panel of Figure 2 (see inset).

**Figure 2.** Left: UV-VIS spectrum of Au@SiO$_2$ solution. Inset: TEM image of Au@SiO$_2$ nanoparticles. Right: UV-VIS spectra of a p-nitrophenol solution with Au@SiO$_2$ particles used for the study.

The UV-VIS spectrum of the coated gold nanoparticles is characterized by absorption between 500 and 600 nm (see Figure 2), due to LSPR (localized surface plasmon resonance) excitation. For details of the synthesis and characterization of the Au@SiO$_2$ nanoparticles we refer to the experimental section and the supporting information (see SI, and Figures S2 and S3).

To check whether the coated nanoparticles are inert, the gold catalyzed reduction of p-nitrophenol was employed as an integral test reaction. For a non-conformal coating of the nanoparticles, the
accessible gold catalyzes the reduction of p-nitrophenol to p-phenylenediamine, i.e., the reduction of the nitro group, leading to a decrease of the absorption of the p-nitrophenol around 400 nm, and the appearance of product absorption at around 310 nm, as shown exemplarily in Figure S2 [31]. No conversion of p-nitrophenol was observed for the Au@SiO₂ nanoparticles employed in this study, as shown in the right panel of Figure 2.

The distance between the gold nanoparticles and the sample is determined by the thickness of the SiO₂ layer. The dependence of the surface-enhanced Raman signal on layer thickness was determined by Li et al. on the basis of the pyridine signal, which decreases with increasing layer thickness [25]. For a layer thickness of more than 10 nm, no signal enhancement was reported. We therefore assume those Au@SiO₂ particles with smaller layer thicknesses to contribute more strongly to the Raman intensity.

In the following, we will discuss the Raman spectra of the LiCoO₂ cathode material, first in the absence and then in the presence of Au@SiO₂ nanoparticles. The left panel of Figure 3 depicts the ex situ Raman spectrum of an as prepared LiCoO₂ composite cathode (yellow line), which is characterized by Raman bands of LiCoO₂ and carbon black. The Raman-active modes of LiCoO₂ result in signals at 486 cm⁻¹ (E₉) and 597 cm⁻¹ (A₁g) [34,35]. The broad bands at around 1340 cm⁻¹ and 1600 cm⁻¹ originate from carbon black in the composite cathode, and are attributed to the defect band (D) and to the C-C stretching mode of graphite (G), respectively [32,33]. The additive PVDF of the composite cathode does not give a contribution to the Raman spectrum of the as prepared cathode, as evidenced by comparison with the spectrum of bare PVDF (see Figure S4).
Figure 3. Left: *Ex situ* (yellow) Raman spectra of a LiCoO$_2$ composite cathode (84% LiCoO$_2$, 8% PVDF, 8% carbon black) and of a LiCoO$_2$ composite cathode with Au@SiO$_2$ particles (red). Quasi *in situ* Raman spectra of a cathode as assembled (black) and cycled (green). The blue spectrum corresponds to Li$_2$CO$_3$ and electrolyte (LP30) in the test cell without Au@SiO$_2$ particles. Right: Detailed view of the carbonate region of the Raman spectra (marked red in the left panel) after background subtraction together with the results of a fit analysis. Spectra were offset for clarity. Raman spectra were recorded with a 632 nm laser.

The LiCoO$_2$ composite cathode containing Au@SiO$_2$ nanoparticles is characterized by the red spectrum in Figure 3. Resembling the spectrum without Au@SiO$_2$ (yellow spectrum), Raman bands of LiCoO$_2$ and carbon black are detected. Please note that no additional signals are observed due to the presence of Au@SiO$_2$ particles, the additive PVDF of the composite cathode, or from any of the precursor compounds (LiNO$_3$, Co(NO$_3$)$_2$, PVP, TEOS, SiO$_2$) (see Figures S5-S7).
In the presence of the electrolyte (LP30), additional electrolyte related Raman signals appear besides the LiCoO$_2$ and carbon related features (see black spectrum) [34,35]. The green spectrum recorded after six cyclovoltammetric cycles at a rate of 0.3 mV/s is dominated by electrolyte signals. It does not contain Raman features of the cathode material in this state of the sample due to the intercalation of the cathode, as described previously [16], and further supported by *in situ* Raman data during cycling (see Figures S8-S10). Besides, no Raman signals due to carbon black are observed, which is attributed to the heterogeneity of the composite cathode, displaying rearrangement on the surface of the composite cathode. In fact, comparison of Raman maps of LiCoO$_2$ composite cathode before and after electrochemical cycling show a redistribution of the chemical composition, due to a rearrangement of carbon additives, as described earlier [32,33]. Interestingly, upon cycling, changes are observed at around 1090 cm$^{-1}$, as indicated in the right panel of Figure 4. Based on a comparison with the spectrum of bare Li$_2$CO$_3$ (see Figures S11 and S12), we attribute the observed feature at 1090 cm$^{-1}$ to the symmetric stretching vibration of carbonate in Li$_2$CO$_3$ [25,36]. As will discussed below, the presence of Li$_2$CO$_3$ indicates the formation or deposition of Li$_2$CO$_3$ on the composite cathode. As shown in the enlarged view of Figure 3, the presence of Li$_2$CO$_3$ is further supported by comparison with the Raman spectrum of a mixture of Li$_2$CO$_3$ and electrolyte (LP30) (see blue spectrum). Please note that the EC electrolyte possesses Raman signals at 1075 and 1085 cm$^{-1}$ [35,37,38]. Thus, for a detailed analysis of this spectral region, all contributions need to be taken into account (see below). Nevertheless, our results demonstrate the presence of Li$_2$CO$_3$ as a component of the SEI after cycling and Raman analysis under quasi *in situ* conditions, i.e., after cycling without exposure to air.

To enhance the understanding of the dynamic behavior of Li$_2$CO$_3$ as a component of the SEI *in situ* surface enhanced Raman spectroscopy was applied directly under electrochemical conditions.
Figure 4 depicts *in situ* Raman spectra of the LiCoO$_2$ composite cathode with Au@SiO$_2$ particles during the first discharging process in the range of 3.4 V to 3.2 V and the second charging process in the range of 3.2 V to 3.4 V. The spectra are dominated by the Raman signals of the cathode and the electrolyte. During the discharge the cathode is intercalated and the E$_g$ signal of LiCoO$_2$ increases. Additionally, as shown in the right panel of Figure 4, a dynamic behavior of the Li$_2$CO$_3$ signal at 1090 cm$^{-1}$ is detected. The detailed view of the carbonate region of the Raman spectra shows the results of a least-square fit analysis of the carbonate Raman signal at 1090 cm$^{-1}$ (orange) and Raman signals of EC (electrolyte) at 1085/1075 cm$^{-1}$ (cyan) together with the resultant of all fit contributions (magenta). For details on the least-square fit analysis please refer to the Experimental section. Initially, no Li$_2$CO$_3$ signal is observed during electrochemical cycling, but during discharging the Li$_2$CO$_3$ signal emerges, and declines during the subsequent charging process. Please note that Li$_2$CO$_3$ has neither been observed in the assembled state of the composite cathode (see Figure 3, black spectrum), nor after storage of the assembled battery (see Figure S13).

The integrated Raman signals are depicted in Figure 5. The Raman signal of Li$_2$CO$_3$ increases during the first discharging cycle, reaches a maximum at 3.2 V, and during the second charging decreases again (see Figures 4 and 5), until it disappears at 3.4 V. Beside the appearance of Li$_2$CO$_3$, no other additional Raman signals are observed during the *in situ* Raman measurements, e.g. from Li$_2$O or LiOH (see Figures S11 and S14). Also there is no indication for the formation of Co$_3$O$_4$, characterized by a signal at 691 cm$^{-1}$ [39], suggesting degradation of LiCoO$_2$ [32].
Figure 4. Left: *In situ* Raman spectra of a LiCoO$_2$ composite cathode (84% LiCoO$_2$, 8% PVDF, 8% carbon black) with Au@SiO$_2$ nanoparticles during the first discharging and second charging process using 632 nm laser excitation. Right: Detailed view of the carbonate region of the Raman spectra after background subtraction together with the results of a least-square fit analysis. Spectra were offset for clarity.

Figure 5. Integrated Raman signals of Li$_2$CO$_3$ (1090 cm$^{-1}$, red points) and EC (1085 cm$^{-1}$, green points, and 1075 cm$^{-1}$, black points) during the first charging, first discharging, and second charging process (blue line). The signals are the result of a least-square fit analysis of the spectra shown in Figures 4 and S8.
Turning to the discussion of the mechanism, the composition of Li₂CO₃ may proceed via different reaction pathways. One possible scenario is based on the reduction of EC and DMC, and the formation of lithium-alkyl compounds (see eq. 1). Li₂CO₃ may be formed starting from (CO₃Li⁻) (see eq. 2) [8,10,11,40-42]. Intermediately formed Li₂O may also react to Li₂CO₃ (see eq. 3) [26].

\[
(\text{CH}_2\text{O})_2\text{CO} + 2e^- + \text{Li}^+ \rightarrow \text{C}_2\text{H}_4 + (\text{CO}_3\text{Li})^- \quad (1)
\]

\[
(\text{CO}_3\text{Li})^- + \text{Li}^+ \rightarrow \text{Li}_2\text{CO}_3 
\]

\[
\text{Li}_2\text{O} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 \quad (3)
\]

\[
\text{H}_2\text{O} + e^- + \text{Li}^+ \rightarrow \text{LiOH} + \frac{1}{2} \text{H}_2 \quad (4)
\]

\[
\text{LiOH} + e^- + \text{Li}^+ \rightarrow \text{Li}_2\text{O} + \frac{1}{2} \text{H}_2 
\]

\[
(\text{CH}_2\text{OCO}_2\text{Li})_2 + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{CO}_3 + \text{CO}_2 + (\text{CH}_2\text{OH})_2 
\]

\[
2 \text{CO}_2 + 2e^- + 2 \text{Li}^+ \rightarrow \text{Li}_2\text{CO}_3 + \text{CO} 
\]

\[
2 \text{HF} + \text{Li}_2\text{CO}_3 \rightarrow 2 \text{LiF} + \text{H}_2\text{O} + \text{CO}_2 
\]

Traces of water can also produce LiOH, Li₂O, and Li₂CO₃ (see eqs. 4-6) [6]. Furthermore, CO and CO₂ formed at the beginning of discharging may also react to Li₂CO₃ (see eq. 7) [6,43]. However, our results indicate the formation of Li₂CO₃ from a lithium-alkyl compound, as no signals of LiOH or Li₂O are detected, in contrast to previous proposals based on ex situ experiments, underlining the importance of direct analysis under electrochemical conditions.

Previously, Hy et al. observed the formation of Li₂CO₃ on LLNMO cathodes during discharging, while intermediately formed Li₂O was observed during charging [26]. It was proposed that
LLNMO materials release oxygen to form Li$_2$O by charge compensation through a combination of Ni$^{2+/4+}$ and Mn$^{3+/4+}$ redox couples. While the authors applied a similar approach to prepare the composite cathode using carbon black and PVDF, a graphite anode was employed as counter electrode and 1M LiPF$_6$ in EC/DEC (ratio 1:1) as electrolyte. Besides, Teshager et al. reported the formation of Li$_2$CO$_3$ on LiCoO$_2$ cathodes during charging above 4.0 V and during discharging below 3.6 V [27]. The authors proposed the decomposition of the EC electrolyte. However, the assigned signals of Li$_2$CO$_3$ are different to those published previously from the same group [44]. On the experimental side, the charging potential of 4.5 V was above the electrochemical window (< 4.3 V) of the electrolyte and cathode, and the circulation of electrolyte differed from a diffusive behaviour of a conventional battery under working conditions. The decomposition of Li$_2$CO$_3$ could be induced electrochemically at higher potential. Hong et al. observed FTIR signals of Li$_2$CO$_3$ appearing and disappearing repeatedly with discharging and charging on Li-excess metal oxides (Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$) [43]. According to the authors, Li$_2$CO$_3$ decomposed to CO and CO$_2$ during charging, as supported by DEMS (differential electrochemical mass spectroscopy) during the charging steps. Besides, Li$_2$CO$_3$ may undergo reactions further, e.g. to LiF (see eq. 8) [43]. HF may be present in the electrolyte due to impurities or decomposition of LiPF$_6$. LiF could also be formed by decomposition of LiPF$_6$ [6,43,45]. LiF should be more resistive than carbonates in the electrolytic environment [8,46]. Due to changes of the chemical composition of the composite cathode during electrochemical cycling as discussed previously [32,33], a rearrangement of Li$_2$CO$_3$ on the surface is possible.
Figure 6. Proposed pathways for (a) Li$_2$CO$_3$ formation during discharging and (b) Li$_2$CO$_3$ decomposition during charging. For details see text.

The proposed pathway of the composition/decomposition of Li$_2$CO$_3$ on a LiCoO$_2$ composite cathode is illustrated in Figure 6. Based on our findings we propose a reaction pathway for the formation of Li$_2$CO$_3$ from lithium-alkyl compounds. Li$_2$CO$_3$ decomposition may proceed via several pathways as discussed above, e.g. by further reaction to LiF, and/or electrochemical decomposition to CO and CO$_2$. The decline of the carbonate Raman signal may also be due to a rearrangement of the surface during electrochemical cycling. In contrast to the results by Hy et al. for LLNMO materials [26], our Raman results suggest that for LiCoO$_2$ composite cathodes other reaction pathways are operative during formation/decomposition of Li$_2$CO$_3$, highlighting the role of the cathode composition. In fact, our findings suggest that the SEI formation originates from electrolyte decomposition. On the other hand, in the presence of Ni or Mn, the cathode material appears to be more reactive than LiCoO$_2$, thus opening different reaction pathways.
4. Conclusions

To increase the sensitivity of in situ Raman spectroscopy for monitoring Li-ion batteries under working conditions, surface-enhanced Raman spectroscopy was applied by using coated gold nanoparticles. Gold nanoparticles were prepared starting from gold chloric acid, coated with SiO$_2$ (Au@SiO$_2$), and checked for conformity by a gold catalyzed test reaction. 

Ex situ and quasi in situ Raman spectra of cycled LiCoO$_2$ composite cathodes, recorded in the presence of Au@SiO$_2$ nanoparticles, showed a carbonate signal at 1090 cm$^{-1}$, besides the signals of the active material (LiCoO$_2$) and the electrolyte, indicating the formation of Li$_2$CO$_3$. Raman experiments under working conditions confirm the formation of Li$_2$CO$_3$ during electrochemical cycling. Detailed analysis reveals the formation and decomposition of Li$_2$CO$_3$, highlighting its role as an intermediate of the SEI. The formation of Li$_2$CO$_3$ is proposed to proceed via electrolyte reduction. The disappearance of the Li$_2$CO$_3$ signal may occur via different pathways, e.g. by reaction to LiF, or electrochemical decomposition, and may also proceed via rearrangement on the surface of the cathode. Our results indicate that Li$_2$CO$_3$ is an intermediate and a component of the SEI on a LiCoO$_2$ composite cathode. Thus, our analysis of the LiCoO$_2$ composite cathode demonstrates the potential of in situ/operando Raman spectroscopy to provide new insight into the SEI formation during operation of Li-ion batteries.

The dynamical aspects of the SEI are highly relevant to the discussion of electrode degradation. To extend the knowledge gained for LiCoO$_2$ composite cathodes, as a next step, the Raman approach could be applied to more complex cathode materials of NMC-type. To further enhance the understanding of the SEI formation on cathode materials, it would also be interesting to systematically introduce Mn and Ni to the composite cathodes, exchanging Co with Mn and/or Ni, in the future.
**Supporting Information**

Details on the synthesis and coating of the gold nanoparticles; Supporting cyclic voltammogram, Raman spectra, and UV-VIS spectra.

**Notes**

The authors declare no competing financial interest.

**Acknowledgments**

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, HE 4515/8-1). The authors thank Dr. S. Lauterbach from the group of Prof. Dr. H.-J. Kleebe (TU Darmstadt) for performing the TEM measurements.
Notes and References


[26] Hy, S.; Felix, F.; Rick, J.; Su, W.-N.; Hwang, B. J. Direct *in situ* observation of Li$_2$O evolution on Li-rich high-capacity cathode material, Li[Ni$_x$Li$_{(1-2x)/3}$Mn$_{(2-x)/3}$]O$_2$ (0 ≤ x ≤ 0.5). *J. Am. Chem. Soc.* **2014**, *136*, 999-1007.

[27] Teshager, M. A.; Lin, S. D.; Hwang, B.-J.; Wang, F.-M.; Hy, S.; Haregewoin, A. M. In situ DRIFTS analysis of solid-electrolyte interphase formation on Li-rich Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ and


[29] Pechini, P. M. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor. US Patent Nr. 3.330.697, **1967**.


[34] By comparison of the Raman signals of the electrolyte from the black spectrum in the presence of Au@SiO$_2$ nanoparticles and the blue spectrum in the absence of Au@SiO$_2$ nanoparticles (see Figure 2), no shift of the Raman signals of the electrolyte is observed due to adsorption on bare gold particles. This is a further indication of the conformity of the Au@SiO$_2$ particles [35].


