

Further identification to the SEI film on Ag electrode in lithium batteries by surface enhanced Raman scattering (SERS)

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Abstract

The surface enhanced Raman scattering (SERS) spectrum of the solid electrolyte interphase (SEI) film on the Ag electrode discharged to 0.0 V in lithium battery was measured by normal Raman spectrometer at different excited wavelength. Compared with the Raman spectra of pure LiOH·H₂O and Li₂CO₃ reagents, all the SERS bands of the SEI film formed on the surface of the Ag electrode can be assigned to Li₂CO₃ and LiOH·H₂O, which are the main stable components of the SEI film in the presence of trace water. LiF may be another possible stable component, however, it cannot be detected due to its inactivity in Raman spectrum. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium batteries; SERS; The SEI film; Ag electrode

1. Introduction

Identification of solid electrolyte interphase (SEI) film formed on the surface of electrodes in lithium ion batteries is essential to understand the relationship between the chemical properties of the SEI film and the electrochemical performance of the electrodes [1]. The SEI film on the surface of anode and cathode has been extensively investigated by FT-IR, HRTEM, SEM, XPS and AFM [2–14]. Recently, we have found that the SEI film formed on the surface of discharged Ag electrode in lithium batteries could be also studied by surface enhanced Raman scattering (SERS) with micro-Raman spectrometer [5,16]. The enhancement is related to the formation of nano-scale Li–Ag alloys. The SERS spectrum is sensitive to the variation of the surface chemical species, surface morphology and discharged state of the Ag electrodes. Up to now, the detection level of SERS technique has come to single-molecule level [17]. It can also provide orientation information of adsorption molecules on electrode surface [16,18]. On the other hand, it has been known that the surface chemistry of Li–C electrode for lithium batteries is similar to that developed on the noble metal electrode polarized to low potentials in the same electrolyte solution [14].

Therefore, we believe that SERS may be a powerful technique to study interface phenomena in lithium ion batteries, especially for understanding the formation mechanism of the SEI film at an early stage. However, in our recent work, most of the SERS bands of the SEI film have not been identified completely except for the assignment of Li₂CO₃.

In this paper, Raman spectra of the Ag electrode discharged to 0.0 V in a lithium battery were recorded by Jobin-Yvon U-1000 Raman spectrometer. The SERS effect of discharged Ag electrode is further confirmed. Compared with the Raman spectra of several referenced compounds, all SERS bands of the Ag electrode are assigned. The formation mechanism of the surface species and resonance Raman effect were further discussed based on these results.

2. Experimental

The preparation of the sample is similar to our previous work [15]. In brief, the silver electrode sheet was covered with the SEI film by discharging a Li/Ag battery to 0.0 V at a constant current density of 0.02 mA/cm² and at this state, nano-scale Li–Ag alloy was also formed. The electrolyte is 1 M LiPF₆ dissolved in ethyl carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) (battery grade, obtained from Beijing Phylion Battery Company). The content of water in this electrolyte was 10 ppm based on the measurement of Karl–Fisher method. The discharged Ag electrode was taken

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out from the lithium battery in an argon-filled M-Braun glove box ($\text{H}_2\text{O} < 1$ ppm), washed by anhydrous DEC ($\text{H}_2\text{O} < 10$ ppm) and dried in vacuum chamber. Then, it was put into a specially designed Raman cell with a sealed quartz window in order to avoid the interference of air during spectral test.

Lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$) (AR, 96% purity with 2% carbonate salts), lithium carbonate (Li_2CO_3) (AR, 99%), lithium fluoride (LiF , AR, >98.5%) are commercial products (Beijing Chemical Reagents Company). Lithium carbonate was heated by vacuum oven before measurement.

Raman spectra were measured by a Jobin-Yvon U-1000 Raman spectrometer at room temperature. The 488.0 and 514.5 nm lines of an Ar^+ laser were used for excitation. The laser power on the samples is about 70 mW.

3. Results and discussion

For comparison, the Raman spectrum of Li_2CO_3 , $\text{LiOH}\cdot\text{H}_2\text{O}$ and LiF as reference compounds are measured at room temperature and shown in Figs. 1–3, respectively. The characteristic bands at 96, 157, 193, 711, 748, 1090,

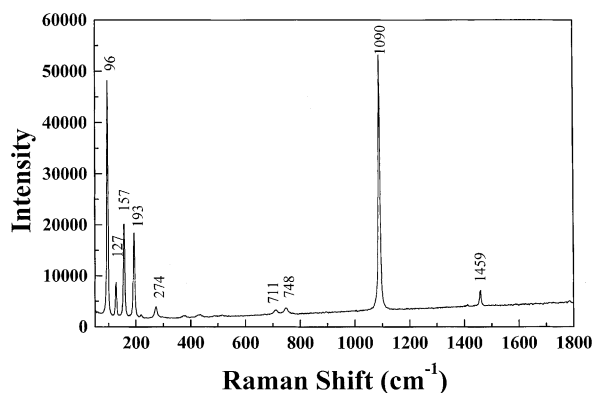


Fig. 1. The Raman spectrum of Li_2CO_3 excited by 488 nm Ar^+ line.

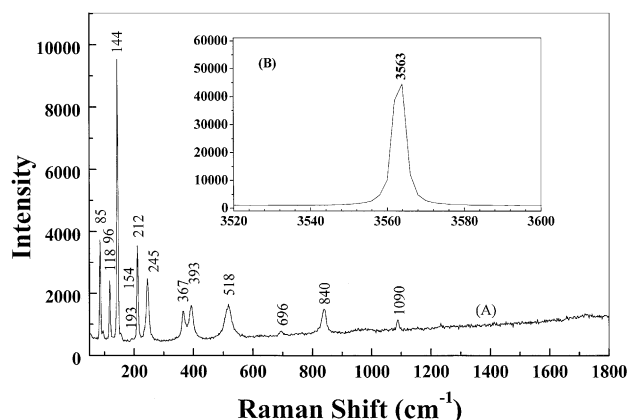


Fig. 2. The Raman spectrum of $\text{LiOH}\cdot\text{H}_2\text{O}$ excited by 488 nm Ar^+ line.

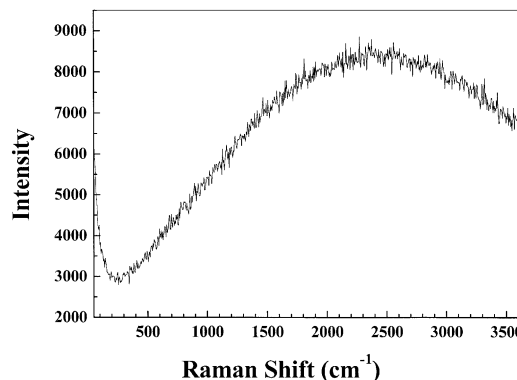
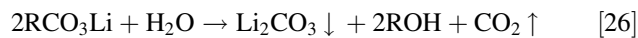
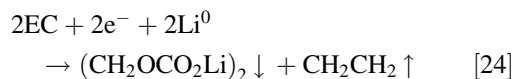
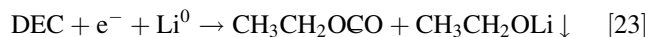
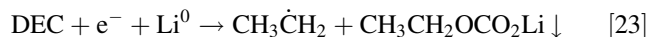
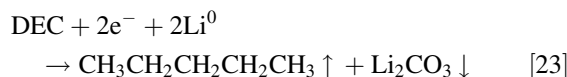
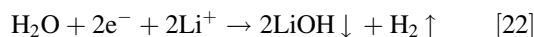


Fig. 3. The Raman spectrum of LiF excited by 488 nm Ar^+ line.

1459 cm^{-1} in Fig. 1 are attributed to Li_2CO_3 , which is similar to the result in reference [19]. Some characteristic bands of Li_2CO_3 at 96, 193 cm^{-1} , especially at 1090 cm^{-1} also appear in Raman spectrum of $\text{LiOH}\cdot\text{H}_2\text{O}$ due to small amount of Li_2CO_3 in original reagent. The strong peak at 3563 cm^{-1} is symmetric OH^- stretching of $\text{LiOH}\cdot\text{H}_2\text{O}$ [20]. No characteristic bands can be observed in the Raman spectrum of LiF in Fig. 3 since bulk crystals show no first-order Raman spectrum [21]. However, it is known that surface-assisted multi-order Raman scattering and surface modes from LiF cluster-based nano-film can be observed. The characteristic bands are located mainly at 120, 300, 408, 614 and 966 cm^{-1} depending on the cluster size (4–7 nm) [21].

Based on the results of FT-IR, the possible reactions for the SEI formation in 1 M $\text{LiPF}_6/\text{EC}-\text{DEC}$ (1:1) electrolyte could be summarized as follows:



Therefore, the solvent (EC and DEC) and solute (LiPF_6) in electrolyte have been reduced during the discharged

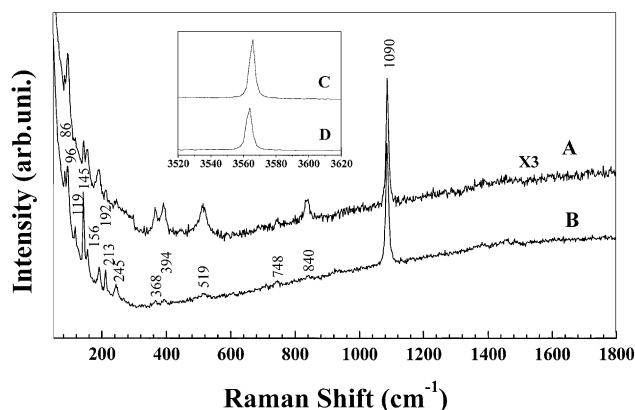


Fig. 4. The SER spectra of SEI film formed on Ag electrode after discharged to 0 V in a Li/Ag cell in which 1 M LiPF₆, EC–DEC (1:1 in v/v) was used as electrolyte. (A) The Raman spectrum excited under 514.5 nm Ar⁺ line. (B) The Raman spectrum excited under 488 nm Ar⁺ line. (C) The Raman spectrum excited under 514.5 nm Ar⁺ line at high wavenumber. (D) The Raman spectrum excited under 488 nm Ar⁺ line at high wavenumber.

process. The reduced species of solvent and solute are the main components of the SEI film. The adsorption of solvent and solute on the electrode surface can be excluded because the characteristic bands of the solvent and solute disappear in the Raman spectrum of the SEI film formed on the electrode surface.

Based on above analysis, for anhydrous electrolyte, the main components of the SEI film are Li₂CO₃, ROCO₂Li, LiF and Li_xPO_y. However, it is inevitable since even the purest non-aqueous solutions contain several parts per million of water. Consequently, the stable species in the SEI film are Li₂CO₃, LiOH and LiF. LiOH may react with water further to form LiOH·H₂O.

The SERS spectra of the discharged Ag electrode are shown in Fig. 4. Though the electrode surface became black after lithium ion inserted into silver electrode, the thermal damage for excitation laser beam is little for the SEI film because the Raman spectrum is about constant after measured for seven times. Compared with Figs. 1–3, it can be seen clearly that the main components of the SEI film formed on the discharged Ag electrode in 1 M LiPF₆/EC–DEC (1:1) electrolyte are LiOH·H₂O and Li₂CO₃. The surface-assisted multi-order Raman scattering modes from LiF cluster-based nano-film are not observed in Fig. 4. It has been known according to XPS data that the SEI film on lithium surface is a multilayer structure. LiF is formed at inner part while Li₂CO₃ and LiOH are existed at outer part [14]. However, the size and distribution of LiF layer or domains in the SEI film are not known till now. Therefore, it can be assumed at least that LiF should not exist in the outer surface since the thickness of the SEI film is usually less than 10 nm [13,14]. But the existence of LiF cannot be excluded.

According to above discussion, the presence of ROCO₂Li is related to the content of water in the electrolyte. ROCO₂Li can be detected by FT-IR [13,14]. Since all bands in Fig. 4 can be assigned to LiOH·H₂O and Li₂CO₃ as listed in Table 1, it seems that ROCO₂Li is absent in this case. But, before drawing this conclusion, it should be confirmed whether ROCO₂Li is SERS active. In our recent paper, the SERS spectrum of discharged Ag electrode in 1 M LiClO₄, propylene carbonate (PC) and dimethyl carbonate (DMC) (1:1 in v/v) electrolyte was also reported [15]. According to current Raman spectra of reference compounds in Figs. 1–3, it is observed that beside the bands related to Li₂CO₃ and PC, some new bands at 442, 565, 1015, 1156, 1248, 1390, 1519, 2130, 2863 cm⁻¹ can be seen in the PC-based electrolyte [15]. These bands do not belong to LiOH·H₂O (see Fig. 1),

Table 1
The assignment of SEI film and comparison to reference compounds^a

SEI film (this work (488 nm))	LiOH·H ₂ O (with Li ₂ CO ₃ impurity)	Li ₂ CO ₃ Ref. [20]	Assignment
86	85		ν_4 [27]
96	95	95	Li ₂ CO ₃ lattice mode
119	118	126	LiO stretching [28]
145	144		ν_6 [27]
156	154	156	Li ₂ CO ₃ lattice mode
192	192	192	Li ₂ CO ₃ lattice mode
213	212		A _g [29]
245	245		OLiO [29]
368	367		OH ⁻ vibration along x-axis [30]
394	393		OH ⁻ vibration “average” over all directions [30]
519	518		T’Li ⁺ vibration [31]
713	696	711	ν_4 (A _g + B _g)
748		748	ν_4
840	840		LiO ₂ Li stretching [32]
1090	1090	1091	A _g
		1459	ν_3 (A _g + B _g)
3563	3563		Symmetric O–H stretching [20]

^a T’: The translational lattice mode.

LiOH [30], LiCl and the electrolyte components [15]. For PC and DMC system, ROCO_2Li is also the main component of the SEI film only with the different alkyl groups [14]. As mentioned above, if the electrolyte is anhydrous, ROCO_2Li will be present while $\text{LiOH}\cdot\text{H}_2\text{O}$ and LiOH will disappear. Therefore, we can draw conclusions that ROCO_2Li is SERS active and most of those new bands belong to ROCO_2Li . In these two cases, the water content in the PC–DMC electrolyte was much lower than it in used EC–DEC electrolyte.

Generally, the identification to $\text{LiOH}\cdot\text{H}_2\text{O}$ in the FT-IR spectra of the SEI film is according to the appearance of O–H stretching vibration mode near 3650 cm^{-1} and Li–O stretch mode around $600\text{--}500\text{ cm}^{-1}$. The first band is weak and always masked by O–H stretching mode of water. The later band is broad and interfered with Li–O stretching mode from ROLi , Li_2O , ROCO_2Li [26]. So, it is not confirmed by FT-IR to decide whether LiOH or $\text{LiOH}\cdot\text{H}_2\text{O}$ exists. Obviously, it is more confident to determine it by SERS according to Fig. 4.

Compared to these results with those spectra obtained from FT-IR [2,13,14], it seems that SERS is more sensitive and confirmative to detect the main components of the SEI film, including Li_2CO_3 , $\text{LiOH}\cdot\text{H}_2\text{O}$ and ROCO_2Li , except for LiF. This will be helpful to clarify the formation mechanism of the SEI film. Considering SERS may be used as an in situ technique, it should be a suitable technique for studying the interface phenomena in lithium ion batteries.

On the other hand, the two SERS spectra of the SEI film under the same measured condition except for the different excited wavelength are slightly different in relative intensity. The characteristic bands of the SEI film in Fig. 4(B) are stronger than those in Fig. 4(A) between 50 and 300 cm^{-1} . The ratio of signal to noise in Fig. 4(B) is better than that in Fig. 4(A). However, the reverse results occur between 300 and 900 cm^{-1} . Because the measured condition in Fig. 4(A) and (B) is completely same, the result indicates that there is different optical absorption behavior of the SEI film under the different excitation wavelength though the other characterization of the SEI film has not been done. Therefore, the results in Fig. 4 should be surface enhanced resonance Raman (SERR) spectrum under 488 and 514.5 nm excitation wavelength because the relative intensity of some SEI bands is distinct under different excitation wavelength. The SERR effect of the SEI film should attribute to the structure of the SEI film. This characteristic of the SEI film contributes to understanding of the SEI structure and interface phenomena.

4. Conclusion

It is confirmed by SERS that the main stable species of the SEI film on the surface of discharged Ag electrode in $1\text{ M LiPF}_6/\text{EC}\text{--}\text{DEC}$ electrolyte are $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2CO_3 . Besides, it cannot exclude the existence of LiF in the SEI film since it is inactive in Raman spectrum. The appearance

of $\text{LiOH}\cdot\text{H}_2\text{O}$ is related to the trace water in the electrolyte. When the water content is very low in an electrolyte, such as 1 M LiClO_4 , PC–DMC (1:1), $\text{LiOH}\cdot\text{H}_2\text{O}$ cannot be detected out and some new characteristic bands at 442 , 565 , 1015 , 1156 , 1248 , 1390 , 1519 , 2130 , 2863 cm^{-1} can be recognized. These bands should be related to ROCO_2Li . Accordingly, SERS is a suitable technique to detect the chemical species of the SEI film in lithium ion batteries. At the same time, the SEI film on Li–Ag alloy electrode show surface enhanced Raman resonance (SERR) effect.

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