

In situ electrochemical studies for Li⁺ ions dissociation from the LiCoO₂ electrode by the substrate-generation/tip-collection mode in SECM

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Abstract This work presents the transportation of Li⁺ ions at the interface of a charging LiCoO₂ electrode through the substrate-generation/tip-collection (SG/TC) feedback mode of scanning electrochemical microscopy (SECM). The TC current, due to the reduction of the ethylene carbonate (EC) supermolecule, is collected more strongly at 1.8 V than that of the Li⁺(DEC)_n at 2.5 V near at the substrate because of the increased concentration of the supermolecule Li⁺(EC)_m, which means that the electrolyte is not uniformly distributed over the substrate. The smooth SG/TC current loop is formed at the probe position optimized by the probe scan curve technique between the LiCoO₂ substrate with 4.0 V and the probe with 1.8 V, which is applied to analyze the Li⁺ ion transport at the interface of the LiCoO₂ electrode. Moreover, the LiCoO₂ substrate, which has a flat surface, is imaged to the nonuniform surface electrochemically by the SECM. We infer that these experimental techniques will help analyze transporting Li⁺ ions at the interface and the electrochemical uniformity of the electrode.

Keywords Li⁺ ion transport · Substrate-generation/tip-collection mode · Scanning electrochemical microscopy · Electrochemical uniform LiCoO₂ electrode · Electrochemical image

Introduction

In the process of charging a Li ion battery, Li⁺ ions dissociate from the LiMO₂ (M=Co, Mn, Ni, etc.) electrode and intercalate into the graphite electrode. The performance of most batteries is dependent on a solid electrolyte interphase (SEI) layer forming at the anode/electrolyte interface and the electrolyte distribution over the electrode surface, because these factors not only decompose the electrolyte but also decrease the transport resistance of Li⁺ ions dissociating from the electrodes. A considerable amount of research effort has been focused on studying the trace of the SEI layer formation using various kinds of spectroscopies and microscopies [1–4]. However, few studies have been published about the electrolyte distribution over the electrode surface even though this is related directly to the rating of a Li ion battery [5]. Recently, we have reported trifluorobenzene as a new additive that has been shown to have a good effect on the high rate properties of Li ion batteries due to the modification of electrolyte distribution over the electrode interface, but not the reformation of the SEI layer [6]. We have also tried to analyze the electrolyte distribution and the Li⁺ ion transportation above the electrode by means of scanning electrochemical microscopy (SECM).

As an electrochemical analysis tool, SECM is very useful because the electrochemical experiments can easily be carried out by the scanning probe in electrolyte solution and be imaged by current unlike other scanning studies. Some instruments, like atomic force microscopy and optical microscopy, can also investigate the sample in an electrolyte solution and have been successfully used to in situ analyze the

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occurrence at electrode surface [7]. However, these microscopes are suitable for the surface topography, not the reactivity of the substrate surface. Usually, the SECM images are dependent on not only the topography but also the surface reactivity of the substrate sample [8]. Therefore, the SECM is much more familiar in the fields of biological and catalytic chemistries which use the substrate with very flat surface [9–11]. Despite the popularity of SECM, however, very few SECM studies have focused on the improvement of the performance of Li ion batteries. Actually, the transport phenomena of Li^+ ions dissociating from LiCoO_2 and graphite electrodes are good research targets for study in the generation/collection (G/C) feedback mode, which is one of the SECM functions. Generally, the G/C feedback mode works in the electrolyte that contains some redox substances around the probe and the substrate. If a reducible substance (O) is generated at the substrate, for example, this substance is reduced at the probe that is located close to the active region of the substrate. Specifically, this mode is called the substrate-generation/tip-collection (SG/TC) mode [12–14]. In an alternative mode, the tip-generation/substrate-collection (TG/SC) mode, the tip is used to generate a reactant that is detected at a substrate electrode. For example, the reduction $\text{O} + \text{ne}^- \rightarrow \text{R}$ occurs at the probe, and the reduced substance is oxidized to a new reducible substance at the substrate: $\text{R} - \text{ne}^- \rightarrow \text{O}'$. Among the many experimental techniques in SECM, the probe scan curve (PSC) technique allows the user to move the probe to the optimum point to measure the substrate effect by the probe current, which is dependent on the substrate state and the electrolyte condition. When the probe is out of the substrate effect, the probe measures the electrochemical reaction only as the mass-transfer-limited current. As the probe approaches the substrate electrode, however, the probe current is affected by the substrate electrode.

In this study, the experimental conditions for study of the Li^+ ion transport from the charging LiCoO_2 electrode to the electrolyte is reported as a new analysis method, including the linear sweep voltammetry (LSV) with the distance from the substrate, the PSC technique, and the SECM image with the charging state. And this transport is checked at the probe as the reduction current of the supermolecule, $\text{Li}^+(\text{ethylene carbonate (EC)})_m$.

Experimental

Electrolyte-grade EC, diethyl carbonate (DEC), and LiPF_6 were received from Technosemichem Co. and were used in this study without further purification. The LiCoO_2 electrode used in this study is a mass-production grade electrode for a Li ion battery, manufactured by Enerland Co. The designed electrolyte system was prepared by volume ratio in a glove

box filled with argon gas (99.999%). All the electrochemical measurements—the LSV, the PSC, and the SECM image—were carried out using an SECM (CHI900B) installed in the glove box. A four-electrode system was adopted in the SECM as shown in Fig. 1: Li metal as the reference electrode, Pt wire as the counter electrode, LiCoO_2 electrode with 3.22-mm radius as working electrode 1, and the SECM probe as working electrode 2. The commercial SECM probe, composed of a Pt wire in a Pyrex capillary tube, had a diameter of 25 μm . Before each experiment, the probe was polished using diamond slurries (15 μm BASI). The scan rates of LSV experiments by the probe were fixed to 50 mV s^{-1} for the peak shape voltogram. The PSC experiments were induced as a scan rate of 0.05 $\mu\text{m s}^{-1}$. The SECM images were measured under the following conditions: 100 μm for the x and y distances, 1 μm for the incremental distance, and 60 $\mu\text{m s}^{-1}$ for the scan rate. SEM investigations of the LiCoO_2 substrate fracture surface were performed using a Mini-SEM (30 kV; SEC SNE-3000M). The conductivity and the viscosity of the electrolyte were measured using the EcoMet conductivity meter with a STEK probe and the Ostwald capillary viscometer, respectively.

Results and discussion

Probe potential for SECM research on the LiCoO_2 substrate

In order to study the transport of Li^+ ions at the interface of LiCoO_2 substrate using SECM, preliminary studies were performed to determine the electrolyte condition with higher conductivity, the oxidation potential of LiCoO_2 particle as the SG condition, the reduction potential of the transporting mediator of Li^+ ions dissociating from the LiCoO_2 particle as the TC condition, and the optimum

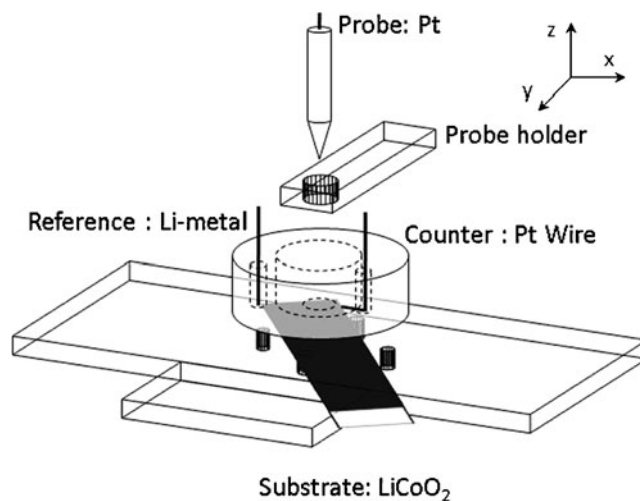


Fig. 1 Schematic of the SECM experimental setup

distance between the substrate and the probe to form the smooth SG/TC feedback loop. The electrolyte condition with high conductivity is an essential precondition to measure the Li^+ ion transport from the charging LiCoO_2 electrode to the probe. The electrolyte conductivity was surveyed with a LiPF_6 concentration in EC/DEC (three of seven). As a result, the conductivity increased to 1.0-M LiPF_6 and decreased beyond 1.0-M due to its higher viscosity. As the electrolyte with higher conductivity was suitable for research on the electrolyte transport in the SG/TC feedback mode, the electrolyte condition with 1.0-M LiPF_6 in EC/DEC=3/7 was selected in this work for good SECM experiments. The potential of the LiCoO_2 substrate was fixed to 4.0 V (vs. Li/Li^+) to balance the feedback loop with the reduction current collecting at the Pt probe with 25 μm diameter, which is near the full-scale oxidation potential to dissociate Li^+ ions from the substrate.

It is not simple to determine whether the probe condition is satisfactory for collecting the electrochemical information generated from the substrate because the TC condition is affected simultaneously by the probe potential and the position from the substrate. The probe should be applied to the potential sufficient to reduce the supermolecule through a smooth SG/TC feedback loop. As shown in Fig. 2a, the two reduction peaks at the Pt disk electrode (0.031 cm^2) were observed at 2.5 and 1.8 V under the described electrolyte condition. In these two peaks, the reduction peak at 1.8 V disappeared in DEC with 1.0-M LiPF_6 (Fig. 2b) but remained in EC with the same concentration of LiPF_6 (Fig. 2c). On the contrary, the peak at 2.5 V disappeared in the EC system but remained in the DEC electrolyte. These results indicate clearly that the peak at 1.8 V is related with the reduction of the EC-solvated supermolecule, $\text{Li}^+(\text{EC})_m$, and the peak at 2.5 V is related with DEC to $\text{Li}^+(\text{DEC})_n$. The reduction source at around

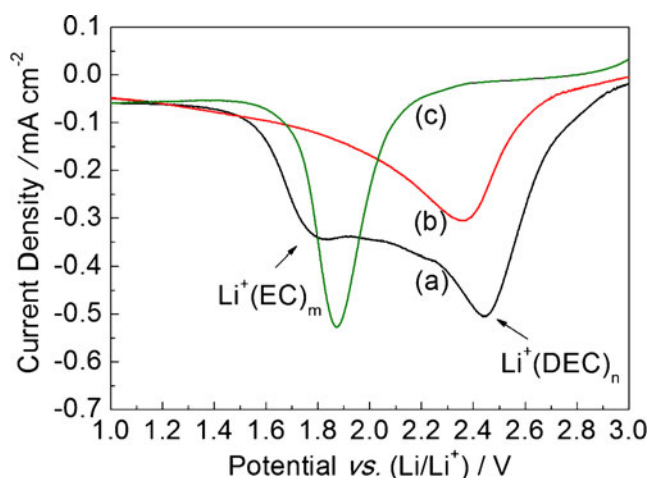


Fig. 2 LSV of various electrolytes on the Pt disk electrode: **a** 1.0 M LiPF_6 in EC/DEC (three of seven), **b** 1.0 M LiPF_6 in DEC, and **c** 1.0 M LiPF_6 in EC (scan rate, 50 mV s^{-1})

2.5 V is also reported as the decomposition of other components such as HF, shown in the electrolyte with a small amount of H_2O as inert [15–17]. As there was no reduction peak at 2.5 V under the EC electrolyte with LiPF_6 , however, we did not discuss the identification of the peak generated at 2.5 V any more in this study. The electrolyte system composed of EC, DEC, and LiPF_6 has been reported to be preferentially solvated as a $\text{Li}^+(\text{EC})_m$ structure, known as the supermolecule [18, 19]. And the reduction potential of this EC supermolecule is also reported to be 1.8 V by Zhuang's group [20], which is defined as the main component of the SEI layer [21–24]. The layer that forms at the interface of the graphite electrode by the reduction of this supermolecule at the first charging process of a Li ion battery is the key component of rechargeable Li ion batteries. From all of these results, the probe potential that is sufficient for study of the Li^+ ions dissociating from the LiCoO_2 substrate was determined to be 1.8 V, the reduction peak of the EC supermolecule, for good SG/TC feedback between the substrate and the probe.

LSV with distance from the LiCoO_2 substrate

The peak shape voltammogram measured by the probe scanning over the LiCoO_2 particles is needed as a prerequisite for the precise SECM study of Li^+ ions transporting at the interface of the LiCoO_2 substrate. Usually, the LSV response on the microelectrode would show a steady-state current curve instead of a peak shape. However, if the scan rate in the LSV experiment is faster than RTD/nFa^2 , we can obtain a peak shape voltammogram even at a microelectrode, where R is the gas constant, T is the temperature, n is the number of electrons transferred during the reaction, F is the Faraday constant, and D is the diffusion coefficient of a reactant. In this report, the diffusion coefficient (D_{EC}) of EC, the main component of the supermolecule transporting Li^+ ions, was calculated to $3.75 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ through the experimental results of the double potential step chronoamperometry [25, 26]. Therefore, one may expect to obtain peak-shaped voltammograms at the reduction potential of the EC supermolecule, if the scan rate at the probe with a 12.5- μm radius is over $0.6 \mu\text{V s}^{-1}$. From these results, the scan rate of all LSV measurements was fixed at 50 mV s^{-1} at the probe in order to maintain a constant state of the electrolyte composition during all experiments in the Ar-charged glove box.

The reduction behavior of these EC and DEC supermolecules was also investigated according to the distance from the LiCoO_2 substrate for the optimum SECM study. In this experiment, a constant potential (4.0 V) was applied to the LiCoO_2 substrate to maintain the dissociating state of Li^+ ions, and the scan rate of the probe was kept to 50 mV s^{-1} for the peak shape voltammogram. As shown in Fig. 3, the current increased at 1.8 V and decreased at 2.5 V

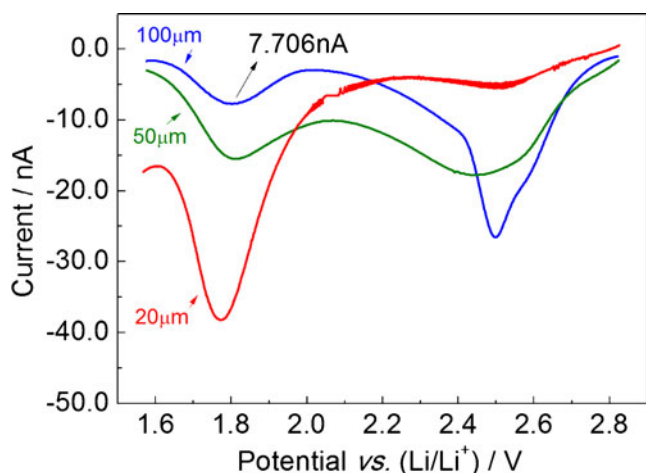


Fig. 3 LSV of 1.0 M LiPF₆ in EC/DEC (three of seven) at the Pt probe according to distance (*d*) from the 4.0 V charged LiCoO₂ substrate (scan rate, 50 mV s⁻¹)

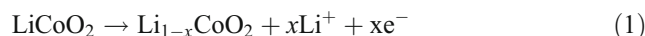
while the probe approached the substrate. These results mean that the concentration of the supermolecule Li⁺(EC)_{*m*} increases near at the substrate and is more easily collected by the probe with 1.8 V than Li⁺(DEC)_{*n*}. Actually, as the dielectric constant of EC (89.6) is much higher than that of DEC (2.86), the Li⁺ ions dissociating from LiCoO₂ substrate will combine preferentially with EC to form a supermolecule system. The reduction current of the characteristic peak (1.8 V) was also calculated to verify the peak identification by the Randles-Sevcik equation [27]: $I_P = (2.69 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}c$, where *n* is the number of transferred electrons (*n*=1), *A* is the area of the working electrode (4.909×10^{-6} cm²), *v* is the scan rate (50 mV s⁻¹), *c* is the reduction species concentration (4.3×10^{-3} mol cm⁻³), and *D* is determined experimentally (3.75×10^{-11} cm² s⁻¹). The constant value, 2.69×10^5 , was calculated at the measurement temperature of 22 °C [28]. The reduction current formed at 1.8 V was calculated as 7.778 nA, matching well with the experimental value (7.706 nA at a 100-μm point from the substrate as shown in Fig. 3). These results indicate once more that the probe current generated at 1.8 V is induced by the reduction of EC supermolecule, and Li⁺ ion transport at the interface of LiCoO₂ electrode could be analyzed through the SG/TC feedback current.

Verification of Li⁺ ion transport by SG/TC mode

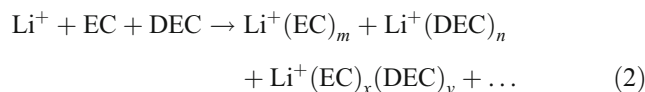
PSC experiments were carried out to decide the optimum position of the probe, where the substrate generation could be properly collected by the probe under the potential conditions of 4.0 V for the substrate and 1.8 V for the probe. As shown in Fig. 4, the probe and the substrate currents remained constant when the probe was far from the substrate. This means that the probe is located out of the

substrate effect and each current is influenced mainly by its reaction type and reaction area. Actually, even though the reaction area of the LiCoO₂ substrate was 66,000 times that of the Pt probe, the current generated at the substrate was only approximately 50 times that of the probe current. This current difference could be inferred from the difference of the reaction type and the potential, the reduction potential (1.8 V) of the EC supermolecule at the surface of the Pt probe, and the oxidation potential (4.0 V) of the LiCoO₂ particles coated on the Al substrate. On the one hand, the probe current increased from approximately a 50-μm point abruptly, prior to the dramatic behavior of the SG current which started to increase from 30 μm. This is one of the forms of evidence of the SG/TC feedback loop, which is formed successively by the dissociation of Li⁺ ions from the LiCoO₂ substrate, the formation of the transporting media, and the reduction of the media at the probe.

Dissociation of Li⁺ ions from the LiCoO₂ substrate as SG process:



Formation of the transporting media as solvation process:



Reduction of the media at the probe as TC process:



Unlike the formation process of the SEI layer on the graphite surface, the Li⁺(EC)_{*m*} supermolecule was reduced

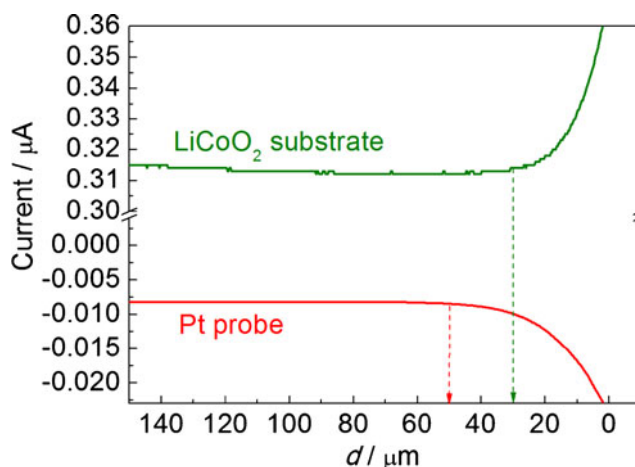


Fig. 4 Current profiles measured by PSC technique in the electrolyte with 1.0 M LiPF₆ in EC/DEC (three of seven) (*d* distance between probe and substrate)

continuously at the Pt probe without any intensity change of the reduction current. This is one of the major experimental steps that enables analysis of the transport of Li^+ ions over the LiCoO_2 substrate by the SG/TC mode of the SECM. That is, the SG current is increased as much as

the supermolecule $\text{Li}^+(\text{EC})_m$ is reduced at the probe, when the probe is approached near the substrate. Therefore, Li^+ ions transporting at the interface of the LiCoO_2 electrode can be analyzed by this SG/TC feedback mechanism, shown by the schematic diagrams of Fig. 5. Note that the PF_6^- ion is not inserted in the schematic diagram. In fact, the PF_6^- ions always exist around the supermolecule system while maintaining charge balance. With an increase of the number m of the supermolecules, $\text{Li}^+(\text{EC})_m$, the interaction between $\text{Li}^+(\text{EC})_m$ and PF_6^- will become weaker because the electronegativity of the supermolecule surface increases. Gradually, the PF_6^- ion becomes easily separated from the supermolecule system around the probe (TC process) and diffuses to recombine with a new supermolecule forming around the substrate. This is one of the mechanisms for formation of the current loop by the SG/TC model. This has been discussed in detail in another study (under preparation) as the major mechanism of the indirect oxidation of the LiCoO_2 electrode.

Verification of electrochemical uniformity of the LiCoO_2 electrode by SECM image

Finally, Li^+ ions dissociating from the LiCoO_2 substrate were imaged by the SG/TC mode of the SECM. As shown in the SEM image of Fig. 6a, the LiCoO_2 particles coat uniformly on the Al sheet with a few projecting particles of about 8- μm diameter (see the projecting particle in Fig. 6a). The probe was scanning at around the 30- μm position from the substrate in SECM experiments—a probe position determined from the PSC experiment. The TC current, however, increased at the special area with increasing the oxidation potential of the substrate from 3.0 to 6.0 V (vs. Li/Li^+) as shown in Fig. 6b. The operating voltage of the LiCoO_2 electrode is generally 3.0–4.2 V because the LiCoO_2 structure is easy to be collapsed beyond 5.0 V in real battery system. Unlike the charging system of the real Li ion battery, however, since SECM was operated in a very short time and with a very weak current, there are few possibilities about this collapse beyond 5.0 V. Actually, as shown in the charging profiles by multi-potential step chronoamperometry in Fig. 6c, no side decomposition curve was shown to the charged state of 6.0 V. These results indicate that the SECM image at each potential means the dissociation ability of the Li^+ ions by the oxidation of the LiCoO_2 substrate. This electrochemical reaction can be varied by the uneven distribution of the LiCoO_2 particles, the binder, and the conducting agent. But there were no special differences on the surface and fracture surface of the LiCoO_2 substrate in the SEM image. Therefore, this stronger current area in the SECM image is certainly induced by the nonuniformity of the electrochemical activity (Li^+ ions dissociating ability) of the LiCoO_2

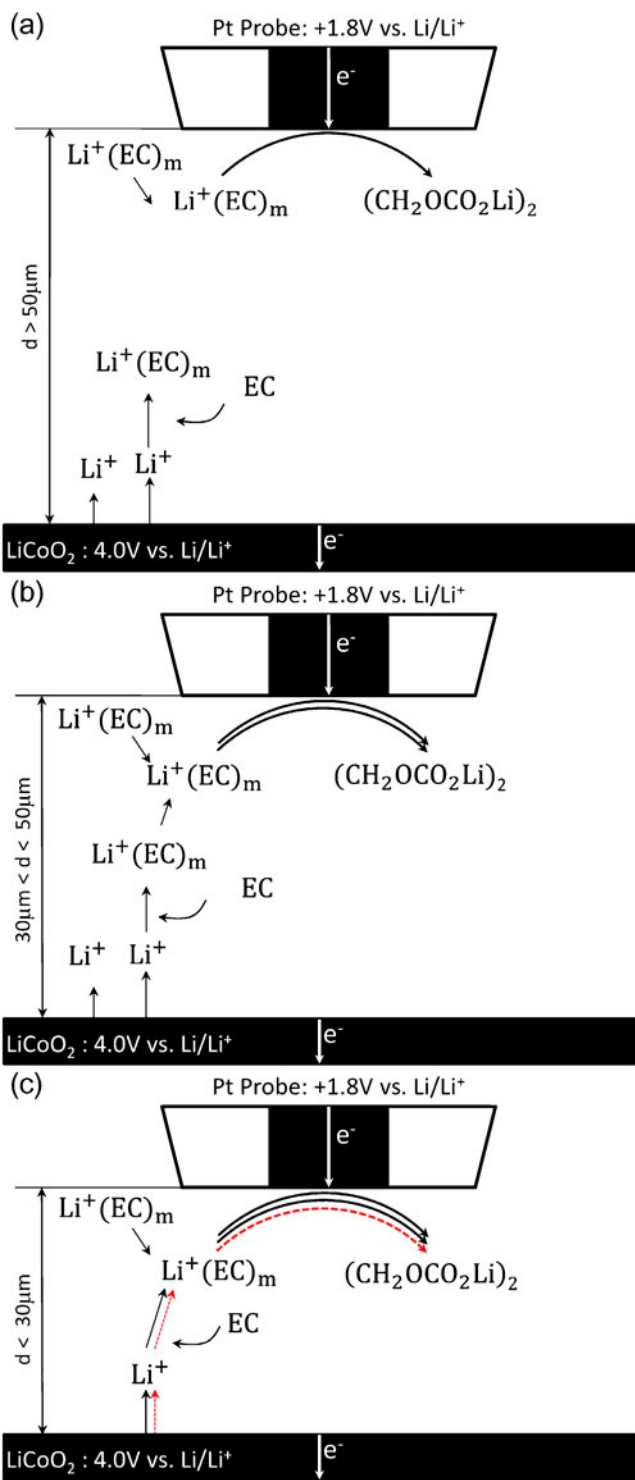


Fig. 5 Schematic diagrams of the SG/TC mode in PSC measurement

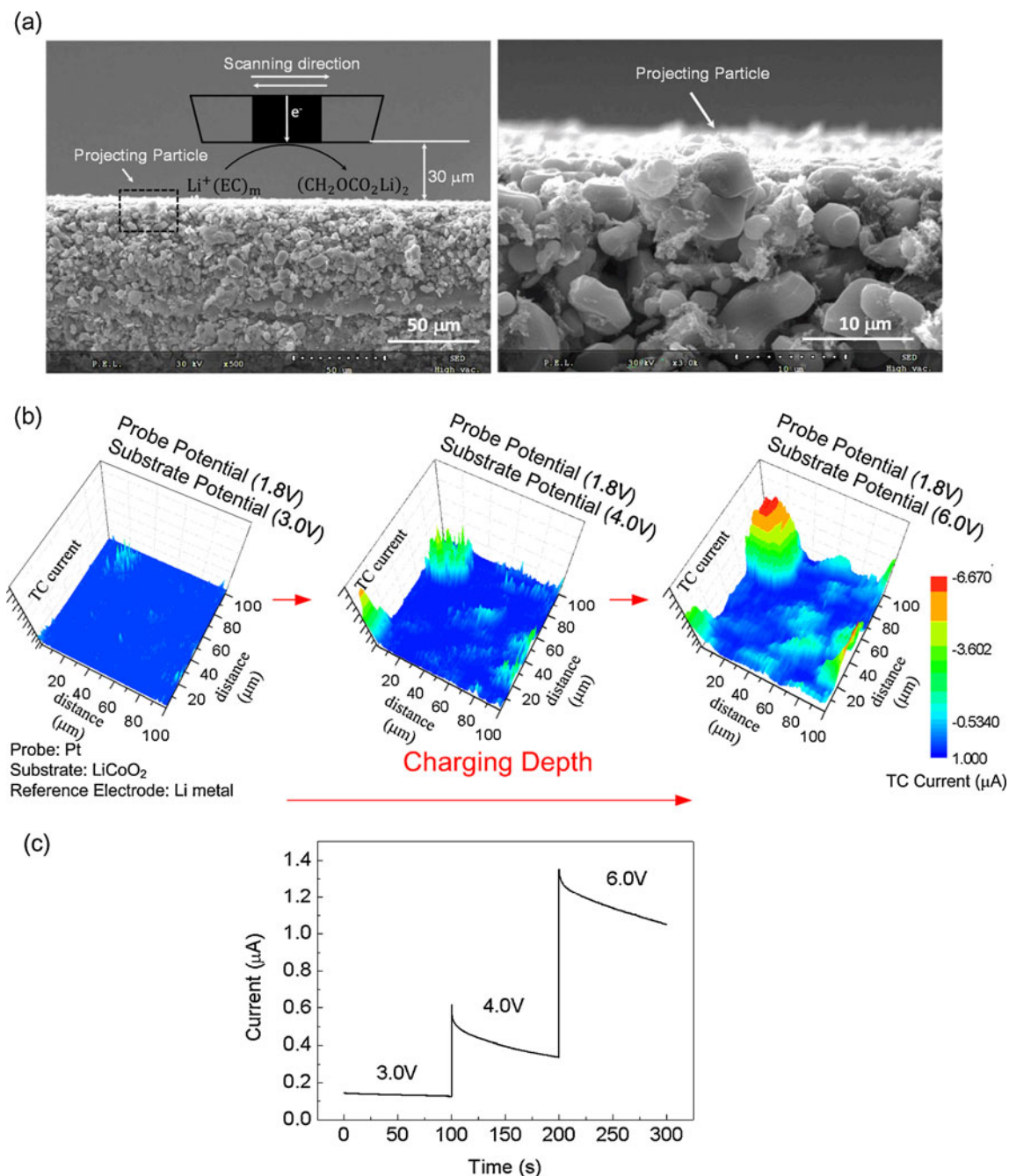


Fig. 6 SEM images of LiCoO₂ substrate (a), SECM images of LiCoO₂ substrate with the charging depth (b), and multi-potential step chronoamperometry of LiCoO₂ substrate applied at 3.0, 4.0, and 6.0 V for 100 s (c)

substrate, not caused by the superficial characteristics of the substrate or other side decompositions. We emphasize that this novel electrochemical analysis method could be applicable to the study of the transport phenomena of electrolyte components in new electrolyte systems (e.g., ionic liquid or gel polymer electrolytes) or the electrochemical uniformity and quality of the fabricated electrode for high-performance Li ion batteries.

Conclusions

The transport of Li⁺ ions at the interface of the charging LiCoO₂ electrode were studied through the SG/TC feedback mode; the experimental conditions were selected and verified by the LSV change according to the distance from the substrate, the PSC technique, and the SECM image with the charging state. As for the SG process, the potential of

the LiCoO₂ substrate was fixed at 4.0 V (vs. Li/Li⁺) to balance the SG/TC loop with the reduction current at the Pt probe, which is near the full-scale oxidation potential for dissociation of Li⁺ ions from the substrate. The reduction peak of the EC supermolecule was stronger at 1.8 V than that of the Li⁺(DEC)_n at 2.5 V near at the substrate because of the increased concentration of the supermolecule Li⁺(EC)_m, which means that the electrolyte is not uniformly distributed over the substrate. The smooth SG/TC current loop was formed at the position optimized by the PSC technique between the oxidation potential of the LiCoO₂ substrate (4.0 V) and the reduction potential (1.8 V) of the EC supermolecule. This experimental method could be applied to analysis of Li⁺ ion transport at the interface of the LiCoO₂ electrode. Finally, the LiCoO₂ substrate, which has a flat surface without projecting particles, was imaged to the nonuniform surface electrochemically by the SECM.

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