

Effects of the electrolyte composition on the electrochemical lithium-intercalation behavior of graphite-analysis by electrochemical quartz crystal microbalance technique

Masayuki Morita ^{a,*}, Tatsuya Ichimura ^a, Masashi Ishikawa ^a, Yoshiharu Matsuda ^b

^a Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755, Japan

^b Department of Applied Chemistry, Faculty of Engineering, Kansai University, 3-5-35 Yamate-cho, Suita 564, Japan

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Abstract

Electrochemical lithium intercalation into graphite and related carbonaceous materials has been investigated in ethylene carbonate (EC)-based organic electrolytes using electrochemical quartz crystal microbalance (EQCM). During constant-current charging (cathodic polarization), changes in the resonance frequency indicated the mass of the electrode increasing generally with an increase in charge passed. The mass change of the graphite per quantity of electricity ($\Delta m \Delta Q^{-1}$) depended on the electrolyte composition in the potential range of 0.0–0.2 V versus Li/Li⁺ as well as in the more positive potential range. Variations in $\Delta m \Delta Q^{-1}$ with electrode potential revealed that the relative rate of electrolyte decomposition yielding precipitation on the graphite surface changes with electrode potential. For the artificial graphite, the mass change in EC + DMC (dimethyl carbonate) containing LiClO₄ was larger than that in EC + PC (propylene carbonate) containing LiClO₄, which suggested that the process in EC + DMC is somewhat different from that in EC + PC. These results are discussed in connection with those obtained from conventional electrochemical and X-ray diffraction measurements. © 1997 Elsevier Science S.A.

Keywords. Lithium-intercalation; Graphite; Organic electrolytes; Electrochemical quartz crystal microbalance technique

1. Introduction

Many carbonaceous materials have been examined for the negative electrode matrices of rocking-chair-type lithium-ion batteries [1,2]. The electrode performance depends on the electrolyte system used in the battery as well as the kind of the carbon material [3]. It is generally accepted that solvents with high reactivity, such as propylene carbonate (PC), are not suited for the batteries using well-crystalline graphite electrodes [4–6]. Ethylene carbonate (EC) seems to be a better solvent for highly graphitized electrodes. In those cases, the electrolytic solutions containing diethyl carbonate (DEC) or dimethyl carbonate (DMC) as a co-solvent of EC show high discharge capability because of their surface chemistry in the electrolyte systems. However, the effects of the electrolyte composition on the electrochemical intercalation process itself are insufficiently understood up to the present.

We have investigated the electrode characteristics of graphite-based and non-graphitized carbon materials in some mixed solvent electrolyte systems [7]. This paper presents

the influences of co-solvents on the cathodic processes of graphite and other carbonaceous materials. Mass changes of the carbon electrodes were monitored during cathodic polarization using an electrochemical quartz crystal microbalance (EQCM). The EQCM technique has already been applied to studies on the electrode processes in battery systems using organic electrolytes. In our knowledge, however, little has been published concerning mass changes for carbon-based negative electrodes during charge and discharge processes in organic electrolytes [8]. We demonstrate here the usefulness of the EQCM technique for analyzing the cathodic processes of the carbon electrode in organic solutions containing lithium salts.

2. Experimental

The electrode materials were powdered artificial graphite (Lonza KS6, the maximum particle size: $\sim 6 \mu\text{m}$, BET surface area: $\sim 20 \text{ m}^2 \text{ g}^{-1}$), turbostratic carbon (Asbury #5645, 325 mesh passed, BET surface area: $\sim 11 \text{ m}^2 \text{ g}^{-1}$) and cal-

* Corresponding author.

cined petroleum coke (Asbury #4023, 325 mesh passed, BET surface area: $\sim 20 \text{ m}^2 \text{ g}^{-1}$). Two types of test electrode were prepared for X-ray diffraction (XRD) and EQCM measurements [8]:

1. For XRD experiments, each carbon powder was mixed with a fluoro-resin binder (14 wt.%) and then molded on a nickel screen current collector to form a thin tablet (bulk electrode, diameter 13 mm, ~ 0.5 mm thick).
2. For EQCM experiments, thin carbon films were coated on a nickel-sputtered quartz crystal piece (AT-cut, diameter 25 mm, $f_0 = 6$ MHz) using a spin coating technique (film electrode). The coating solutions were carbon/cyclohexane slurries containing 2 wt.% EPDM (ethylene/propylene/diene monomer) binder. The resulting quartz crystal was loaded with about 0.1 mg cm^{-2} of the carbon powder.

The electrolytes were mixed solvent systems based on EC with PC, DMC or DEC as the co-solvents (EC + PC, EC + DMC and EC + DEC; 50 + 50 by volume). These were used as received from Mitsubishi Chemical (battery grade). Dehydrated LiClO_4 or $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ as the electrolyte salt was dissolved in the mixed solvents to yield 1.0 M solutions.

A glass beaker cell (50 cm^3) was used for electrochemical measurements using the bulk electrode. The reference and the counter electrodes were a lithium chip in the test solution and a large surface area lithium sheet, respectively. The performance of the electrode was examined by constant-current charge and discharge cycling (usually 0.14 mA cm^{-2}). XRD was carried out for the electrodes after each charge and discharge cycle.

A cylindrical Teflon cell (about 50 cm^3 volume) equipped with an oscillator unit (Hokuto Denko HQ-301) was used for the EQCM experiments. The carbon-coated quartz crystal piece was mounted at the bottom of the cell. A lithium chip reference and lithium sheet counter electrodes were set above the test electrode. The resonance frequency (f) of the quartz crystal was monitored with a frequency controller unit (Hokuto Denko HQ-101B) during constant-current polarization. The mass change on the quartz crystal was estimated by Sauerbrey's equation [9].

3. Results and discussion

As the cathodic polarization of carbon electrodes corresponds to the charging process in real batteries, we refer to the process as 'charging' and the reverse (anodic) as 'discharging' in this paper. Fig. 1 shows typical EQCM results obtained for the graphite (KS6) electrode in three electrolyte solutions. The changes in the electrode potential and the resonance frequency are plotted versus the specific charge (charging capacity, quantity of electricity passed: Q under the constant-current ($30 \mu\text{A cm}^{-2}$) polarization. The charge consumed for full charge (to 0 V) depended on the electrolyte

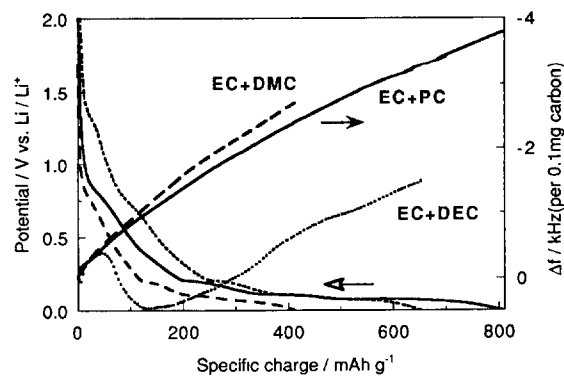


Fig. 1. Potential and frequency changes with charging capacity for graphite (KS6) in three electrolytes containing 1 M LiClO_4 : (—) EC + PC; (---) EC + DMC, and (· · ·) EC + DEC.

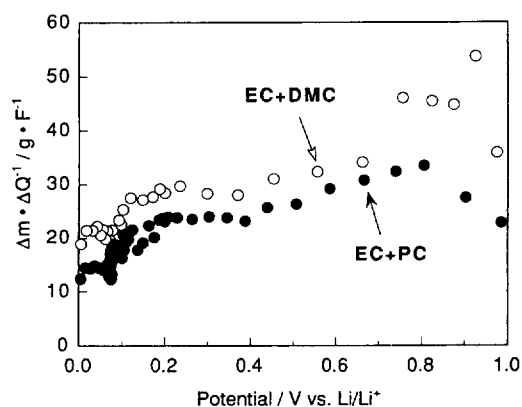
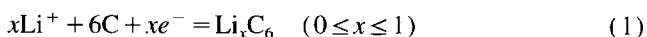
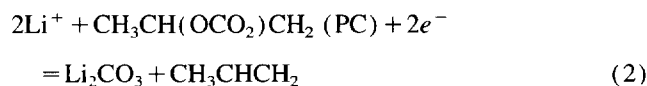


Fig. 2. Variations in $\Delta m \Delta Q^{-1}$ vs. E for graphite (KS6) in two electrolytes containing 1 M LiClO_4 : (●) EC + PC, and (○) EC + DMC.

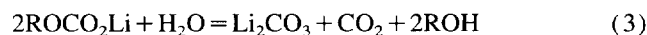
composition. The frequency change ($\Delta f = f - f_0$) decreased monotonously with the charging capacity for the polarization in EC + PC and EC + DMC, whereas the Δf in EC + DEC showed a rather complicated profile. The mass change per quantity of electricity passed ($\Delta m \Delta Q^{-1}$) was evaluated from the frequency change using Sauerbrey's equation [9]. In Fig. 2, the mass changes obtained in EC + PC and EC + DMC are plotted versus the electrode potential. If the cathodic reaction consisted of a simple lithium intercalation (Eq. (1)), the mass increase, $\Delta m \Delta Q^{-1}$, should be 6.94 g F^{-1} ($F = 9.65 \times 10^4 \text{ C mol}^{-1}$)



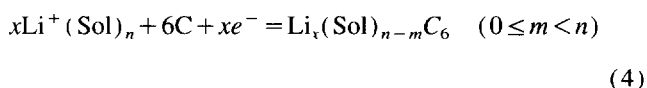
In the potential region above 1.5 V versus Li/Li^+ , very high values of $\Delta m \Delta Q^{-1}$ were observed for both EC + PC and EC + DMC. The values of 27–35 g F^{-1} in the potential range of 0.5–0.8 V in EC + PC suggest that, at least, another reaction proceeds in this potential region. For example, decomposition of the solvent PC yielding precipitation of Li_2CO_3 (Eq. (2)) would lead to a mass increase of 36.9 g F^{-1} on the graphite surface



In PC-based solutions, Aurbach et al. [10] detected some organic carbonates on graphite surface by FT-IR spectroscopy. In that case, the mass change should be higher than the value of 36.9 g F^{-1} . Thus, the observed mass change being lower than that expected from reaction (2) would be due to the conversion of the organic carbonate to lower molecular weight compounds as Li_2CO_3 which may occur through a reaction with trace water in the system (Eq. (3)) [11]



We assume that some competitive reactions occur on the graphite surface as well as lithium incorporation in the graphite bulk under these polarization conditions. As $\Delta m \Delta Q^{-1}$ decreased slightly with decreasing in the potential, the process probably depends on the electrode potential. A minimum $\Delta m \Delta Q^{-1}$ value was observed at the potential below 0.1 V in EC + PC, but was about 15 g F^{-1} . This means that, even at such low positive potentials, the cathodic lithium intercalation into graphite structure is accompanied by some side reactions like Eq. (2). As another possibility solvent co-intercalation [12,13] may be a cause of the $\Delta m \Delta Q^{-1}$ values higher than the theoretical value of 6.94 g F^{-1} . Since the observed $\Delta m \Delta Q^{-1}$ values are much lower than that expected from the molecular weights of the solvents, even in that case, lithium insertion accompanied with no solvent molecule (Eq. (1)) would proceed in parallel with the lithium insertion with solvent co-intercalation (Eq. (4))



The mass change observed in EC + DMC was apparently higher than that in EC + PC. Yoshida et al. [14] detected CH_3OLi as a cathodic decomposition product on the graphite surface in DMC-based electrolytes. The EQCM result may reflect such a difference in kind of the decomposition product on the graphite surface depending on the kind of organic solvent.

Figs. 3 and 4 show the comparison of the XRD patterns obtained for the bulk graphite electrode before and after the constant-current charging and discharging in EC-based electrolytes. The XRD patterns showed the formation of graphite intercalation compounds (GICs) mainly with a stage-2 structure (LiC_{12}) after the first charging process in EC + PC (Fig. 3). The electrochemical intercalation/de-intercalation process in this electrolyte system was generally reversible, as shown in the XRD patterns after the subsequent cycles. The difference in the charges observed in the first charging process shown in Fig. 1 (about 800 mA h^{-1}) and expected from the XRD patterns (LiC_{12} ; about 186 mA h^{-1}) means that the first charging process in EC + PC includes some surface proc-

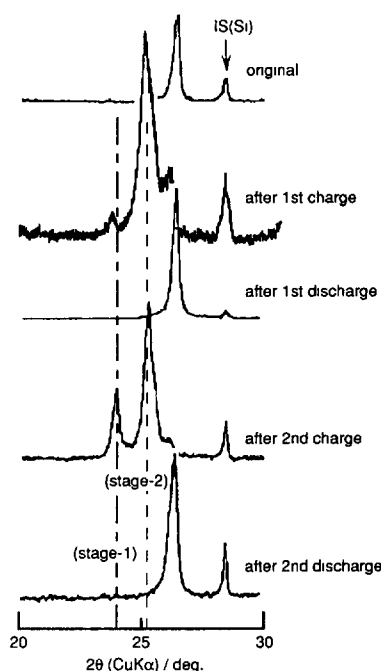


Fig. 3. XRD patterns for graphite (KS6) after charge/discharge cycles in 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$.

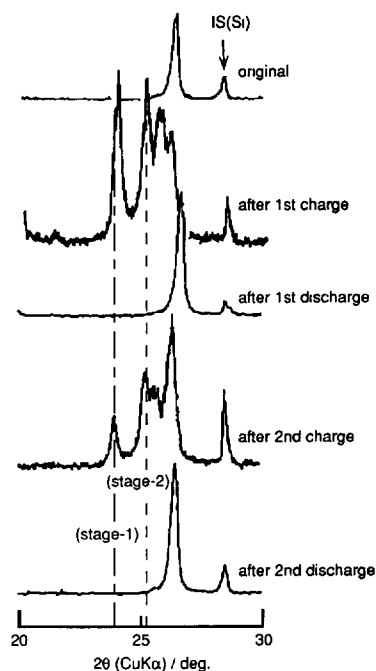


Fig. 4. XRD patterns for graphite (KS6) after charge/discharge cycles in 1 M $\text{LiClO}_4/\text{EC} + \text{DMC}$.

esses that would not be reflected in the XRD patterns. On the other hand, the charging in EC + DMC gave a rather complicated diffraction pattern (Fig. 4). The main peak at $d_{002} = 0.368 \text{ nm}$ was not ascribed to any staged structures of

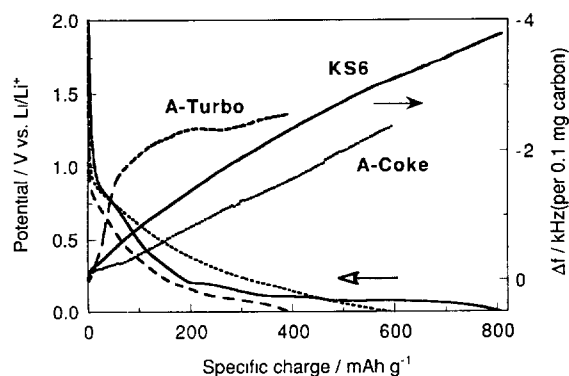


Fig. 5. Potential and frequency changes with charging capacity for graphite (KS6), turbostratic carbon (A-Turbo) and petroleum coke (A-Coke) in 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$: (—) graphite (KS6); (---) turbostratic carbon (A-Turbo), and (· · ·) petroleum coke (A-Coke)

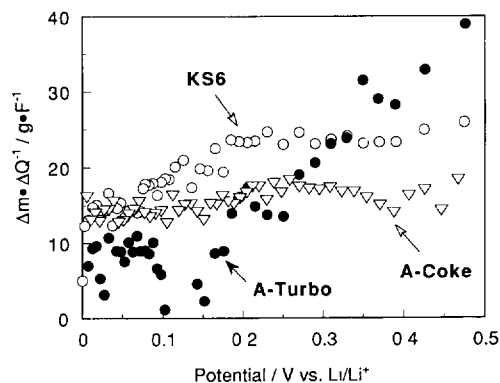


Fig. 6 Variations in $\Delta m \Delta Q^{-1}$ vs. E for (○) graphite (KS6), (●) turbostratic carbon (A-Turbo) and (▽) petroleum coke (A-Coke), in 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$

Li-GICs. Another peak was also observed at higher diffraction angle than that based on the stage-2 structure. However, the XRD pattern after discharging proved the process is essentially reversible. We conclude that the electrochemical Li intercalation into graphite from EC + DMC might be accompanied by co-intercalation of the solvent molecule or a fragment of the decomposed solvent [13].

The EQCM experiment was done for different carbon materials. Fig. 5 gives the variations in the electrode potential and the frequency change (Δf) for the graphite (KS6), the turbostratic carbon (A-Turbo) and the calcined petroleum coke (A-Coke) during the first charging in 1 M $\text{LiClO}_4/\text{EC} + \text{PC}$. In Fig. 6 the variation in $\Delta m \Delta Q^{-1}$ with the electrode potential are shown. The mass change at the petroleum coke was almost the same as that at the graphite in the potential region below 0.1 V. However, the values for the petroleum coke was significantly lower than those for the graphite in the potential region above 0.2 V. This is probably due to the fact that the rate of the cathodic decomposition is much

lower at the surface of cokes with less amounts of the graphite edge face than at the artificial graphite surface. On the other hand, the turbostratic carbon gave a unique mass change profile in the potential region of 0.2 to 0.1 V, where $\Delta m \Delta Q^{-1}$ was apparently zero. Almost the same profile was obtained for the turbostratic carbon in EC + DMC. These suggest that a somewhat different process occurs at this type of carbon material. Some electrochemical processes including no mass change, e.g. $\text{Li}(+1)$ to $\text{Li}(0)$ in the solid phase, might explain these phenomena.

The effects of the electrolyte salt were also observed on the EQCM response of the graphite (KS6). The mass changes ($\Delta m \Delta Q^{-1}$) in the potential region below 0.1 V were 7–10 g F^{-1} in the solutions of EC + DMC and EC + DEC containing 1 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, whereas $\Delta m \Delta Q^{-1}$ in the solutions containing 1 M LiClO_4 varied in the range of 15–25 g F^{-1} (see Fig. 2). The lower values of the mass change in $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ solutions seemed to relate with higher coulombic capacities of the graphite-based negative electrode in $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ solutions [15]. Details in the effects of the salt on the charge/discharge performance of the graphite-based negative electrode are now under investigation.

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