



Effects of electrolyte-volume-to-electrode-area ratio on redox behaviors of graphite anodes for lithium-ion batteries



Sung-Jin Kang^a, Sunghun Yu^b, Chulhaeng Lee^b, Dookyong Yang^b, Hochun Lee^{a,*},¹

^a Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 711-873, South Korea

^b Batteries R&D, LG Chem Ltd., Daejeon 305-380, South Korea

ARTICLE INFO

Article history:

Received 13 May 2014

Received in revised form 1 July 2014

Accepted 16 July 2014

Available online 31 July 2014

Keywords:

Li-ion batteries

Graphite

Solid electrolyte interphase

Electrolytes

Lithium salt.

ABSTRACT

This study reports on the crucial effects of the ratio of electrolyte volume to electrode area on redox reactions of graphite anodes for lithium-ion batteries (LIBs). It is found that a pyrolytic graphite edge plane electrode (PGE) exhibits reversible Li^+ transport behavior in LiClO_4 solution, but shows a suppressed redox reaction in LiPF_6 electrolyte. The reversible Li^+ transport in LiClO_4 is hampered by the presence of trace HF, while the depressed activity in LiPF_6 is improved by adding an HF scavenger, which points to the suppressive effects of HF on the redox behavior of PGE. In addition, the redox activity of PGE in LiPF_6 solution is either enhanced by decreasing electrolyte volume or diminished by decreasing surface area. It is also revealed that graphite composite electrodes of practical LIBs are also subject to the influence of HF if an excessive amount of electrolyte is employed. These observations are attributed to the HF-induced formation of a passive LiF layer, which is facilitated at high ratio of electrolyte volume to electrode area. Our results clearly demonstrate that HF impurity significantly suppresses the redox activity of graphite anodes, and that the adverse HF influence becomes predominant at a high electrolyte-to-electrode ratio.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Highly ordered pyrolytic graphite (HOPG) has long served as a model system for graphite anodes of lithium-ion batteries (LIBs). It has provided valuable information on solid electrolyte interphase (SEI) formation/degradation, morphological change of the anode surface, and Li^+ ion transport kinetics [1–7]. Intriguingly, most HOPG experiments have been performed in LiClO_4 -based solutions [1–7], rather than in LiPF_6 electrolytes, which is more relevant to practical LIBs. The reason for the huge preference for LiClO_4 over LiPF_6 in HOPG studies has yet to be clarified.

LiPF_6 -based electrolytes inevitably contain a trace amount of HF, a byproduct of LiPF_6 hydrolysis [8–10]. Regarding the effects of HF on SEI formation, Aurbach et al. addressed the peculiar characteristics of LiPF_6 electrolytes compared with those of LiAsF_6 or LiClO_4 solutions [11]. They claim that solvent reduction product such as ROCO_2Li is a major SEI component of graphite electrodes in LiAsF_6 or LiClO_4 solutions. On the other hand, in LiPF_6 solution, the organic SEI component is gradually replaced by LiF and other

salt reduction products; this replacement process is induced by the interaction with HF [11]. Recently, Tang et al. also reported that the SEI formed on HOPG shows more unstable behavior in LiPF_6 solution than it does in LiClO_4 electrolyte [5,6]. In addition, Nakagawa et al. reported that the surface crystallinity of graphite is degraded more rapidly in an LiPF_6 -based electrolyte than in an LiClO_4 -based electrolyte [7].

The unstable nature of the SEI derived in LiPF_6 -based electrolytes is quite unexpected because LiPF_6 is being commonly adopted in the current LIB industry. To address this dilemma, the ratio of electrolyte volume to electrode surface area (hereafter called the electrolyte-to-electrode ratio) has been suggested as a topic of research [5–7,11]. Commercial LIBs employ porous graphite composite electrodes, which have much larger surface areas, and accommodate smaller amounts of electrolyte than do the flooded cells commonly adopted for HOPG experiments. Accordingly, the electrolyte-to-electrode ratio is much smaller in commercial LIBs, and therefore the effects of HF contaminant are less pronounced than in flooded cells. This postulation, however, has yet to be supported by experimental evidence.

This study investigates the Li^+ transport behavior of a pyrolytic graphite edge plane electrode (PGE) in LiPF_6 solutions, comparing it to the Li^+ transport behavior in LiClO_4 solutions. In particular, the impact of the electrolyte-to-electrode ratio on the redox

* Corresponding author.

E-mail address: dukelee@dgist.ac.kr (H. Lee).

¹ ISE member

reaction of PGE is examined through deliberate control of the electrolyte volume or the electrode surface area. Then, the implications deduced from the PGE experiments are extended to commercial grade graphite composite electrodes, in order for this research to be relevant for practical applications. This study offers a possible explanation for a decades-old puzzle: why the adverse effects of HF on graphite anodes commonly present in flooded cells are absent in practical LIBs.

2. Experimental

2.1. Chemicals

LiClO_4 (99.99%), HF (48 wt% in water), and hexamethyl disiloxane were purchased from Aldrich. Battery grade ethylene carbonate (EC), diethyl carbonate (DEC), and 1 M LiPF_6 EC/DEC (1/2, v/v) were provided by LG Chem.

2.2. Electrochemical measurements

A standard three-electrode configuration in a flooded cell (polyethylene round bottle, 22 mm diameter) with 4 ml of electrolyte was employed, otherwise mentioned. Li and Pt wire served as reference and counter electrodes, respectively. A pyrolytic graphite edge plane electrode (PGE, area = 0.07 cm^2) from ALS (Japan) and a graphite composite electrode were used as the working electrode. Cyclic voltammetry (CV) was performed over 3.5–0.0 V at a scan rate of 5 mV s^{-1} , otherwise mentioned. The base electrolyte was 1 M LiClO_4 or 1 M LiPF_6 in EC/DEC (1/2, v/v). For the CV experiment, which had a small electrolyte amount, a two-electrode configuration was employed. A Li disk (14 mm diameter), serving as reference and counter electrodes, was covered with a polyethylene separator (Tonen, $20 \mu\text{m}$ thick) and soaked with 0.04 ml of electrolyte; on top of this, the PGE was placed so as to gently touch the separator. PGE was polished on emery paper (#3000, $7 \mu\text{m}$ grit size) or with alumina ($0.3 \mu\text{m}$ diameter) slurry on a polishing pad. After the mechanical polishing, PGE was rinsed with distilled water in the ultrasound bath for 1 min to avoid any possible contamination by emery or alumina powder. Hereafter, the PGE are called emery-PGE and alumina-PGE, respectively. Surface area of emery- or alumina-PGE was estimated from the double-layer capacitance, C_{dl} . The CVs of PGE were obtained in aq. 1.0 M KCl with a Ag/AgCl reference and Pt counter electrode. C_{dl} was calculated from the slope of the steady-state current versus the scan rate [5]. The potential limits were $\pm 50 \text{ mV}$ from the open-circuit potential, and the scan rate ranged from 0.5 to 5.0 V s^{-1} .

The graphite composite electrode was fabricated with artificial graphite (DAG-87, Sodiff) with 1.5 wt% styrene-butadiene rubber (SBR) and 1 wt% carboxymethyl cellulose (CMC) on Cu foil ($20 \mu\text{m}$ thick), with two different loading levels: 6.9 mg cm^{-2} for the thicker electrode and 1.9 mg cm^{-2} for the thinner one. The coated composite electrode was cut into a size of 0.25 cm^2 , to which a SUS strip wrapped with insulating imide tape was welded in order to serve as an electrical lead. Electrochemical experiments were carried out with a VSP potentiostat (BioLogic). Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range from 100 kHz to 20 mHz with an amplitude of 5 mV. All the electrochemical experiments were performed in an Ar-atmosphere glove box in which H_2O and O_2 concentrations were kept below 5 ppm and temperature was held at $25 \pm 1 \text{ }^\circ\text{C}$.

X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250Xi (Thermo Scientific) with a monochromatic Al K α source. Samples were prepared in an Ar-atmosphere glove box. The graphite composite electrodes were subjected to ten CV cycles in a flooded cell with 1 M LiPF_6 EC/DEC

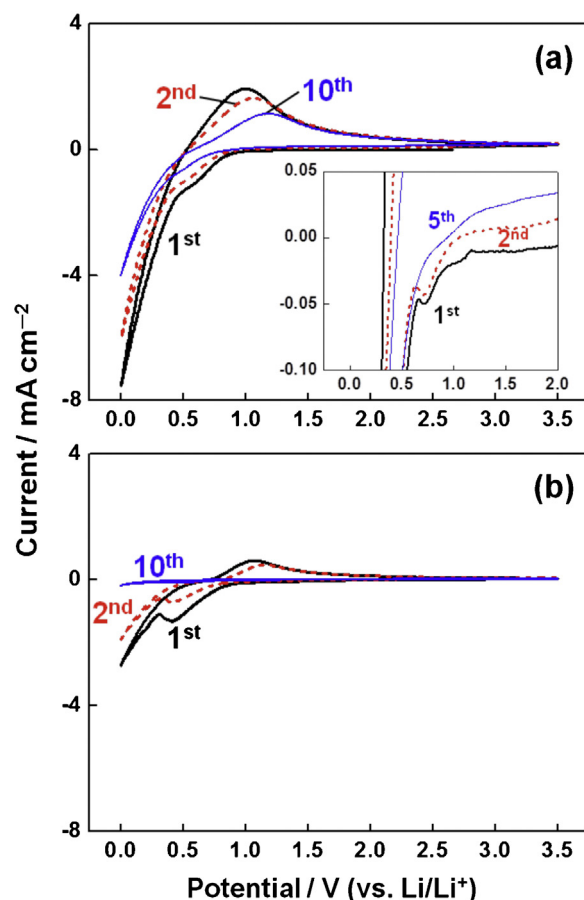


Fig. 1. Cyclic voltammograms of emery-PGE in a flooded cell with (a) 1 M LiClO_4 and (b) 1 M LiPF_6 EC/DEC (1/2, v/v). Inset in Fig. 1a: an enlarged view of the CV obtained at a scan rate of 0.1 mV s^{-1} in 1 M LiClO_4 .

(1/2, v/v) solution, and rinsed with pure dimethyl carbonate to remove residual salt. Before the sample transfer from a glove box to a XPS vacuum chamber, the electrodes were sealed with an aluminum pouch bag under a vacuum. Then, the samples were rapidly transferred from an aluminum pouch into the XPS vacuum chamber to minimize any possible contamination. The electrodes were briefly (20 s) exposed to air during transfer to the XPS chamber. The binding energy was calibrated from the C 1s peak at 285.1 eV. The XPS curve fittings were performed using the Thermo Avantage program with Gaussian–Lorentzian functions (30% L/G mix product) after subtraction of a smart background. The relative error in the fitting method employed in this study is within $\pm 1\%$.

3. Results and discussion

3.1. Suppressive effects of HF on redox behaviors of PGEs

The cyclic voltammograms (CVs) of emery-PGE in 1 M LiClO_4 and 1 M LiPF_6 EC/DEC (1/2, v/v) solutions are compared in Fig. 1. The CV measurements were made in a flooded cell with an excessive amount (4 ml) of electrolyte. In LiClO_4 (Fig. 1a), the reduction current starts to flow below 0.9 V during the 1st cathodic sweep, and an oxidation peak is observed at 1.0 V during the following anodic sweep. The redox activity is maintained even after 10 consecutive CV cycles, which manifests the reversible nature of Li^+ transport in LiClO_4 . The reduction and oxidation currents are obviously assigned to the intercalation and the deintercalation of Li^+ ion through PGE, respectively [1–7]. No reduction current due to solid electrolyte interphase (SEI) formation is discernible during

Download English Version:

<https://daneshyari.com/en/article/185311>

Download Persian Version:

<https://daneshyari.com/article/185311>

[Daneshyari.com](https://daneshyari.com)