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Anodic behavior of stainless-steel substrate in organic electrolyte solutions containing different lithium salts

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ABSTRACT

The anodic behavior of austenitic stainless-steel, SUS304, as a current collector of positive electrode in lithium-ion battery/capacitor has been investigated in organic electrolyte solutions based on a mixed alkyl carbonate solvent with different lithium salts. Stable passivation characteristics were observed for the stainless-steel in the $LiPF_6$ solution, but pitting corrosion or active dissolution proceeded in the solutions containing other anions, BF_4^-, $(CF_3SO_2)_2N^-$ ($TFSA^-$) and ClO_4^-. The mass ratios of the dissolved metal species in the solutions of LiTFSA and $LiClO_4$ were equivalent to that of the alloy composition, which suggests that no preferential dissolution occurs during the anodic polarization in these electrolyte solutions. An HF component formed by decomposition of PF_6^- with the contaminate water will act as an F^- source for the formation of a surface fluoride layer, that will contribute to the anodic stability of SUS304 in the $LiPF_6$ solution. The anodic corrosion in the LiTFSA solution was suppressed in part by mixing the PF_6 salt or adding HF in the electrolyte.

1. Introduction

Hybrid capacitor systems consisting of a capacitor electrode and a battery electrode with proper electrolyte solutions have been developed as advanced electrochemical energy-storage devices in wide application area. A typical system using an activated carbon positive electrode and a graphite negative electrode, which is also called “lithium-ion capacitor (LIC)”, has higher specific capacitance than conventional electric double-layer capacitors (EDLCs) and higher rate capability than lithium ion batteries (LIBs). Such an electrode combination enables higher operation voltage, and thus leads to higher energy density than that of conventional EDLCs [1–4]. In these electrochemical energy devices, aluminum (Al) is commonly used as current collectors of the positive electrodes, because of its light weight, high electronic-conductivity, reasonable mechanical strength, and corrosion-protective properties in organic electrolyte solutions [5,6]. From the viewpoint of the safety issue, however, the Al current-collector has serious problem that should be taken into account when the device is applied to a larger size of the system. Santhanagopalan, *et al.* reported that the Al current collector will be a major source of thermal runaway of LIB when a fully charged device is short-circuited in abuse [7]. Thus, it has been an important issue to replace Al by a proper metallic conductor that should have no or minimum risk of exothermic reaction even if the cell is unexpectedly short-circuited.

Up to the present, extensive research work has been made to develop substituent materials for Al as the positive electrode current-collector in LIB systems. Stainless-steel would be the most possible candidate of the current-collector because of its chemical and electrochemical stability in organic media as well as its tunable composition of iron-based alloy [8,9]. With respect to the Al current-collector presently used, several research groups have so far published papers on the anodic characteristics in organic electrolyte solutions [5,6,9–14]. However, there has been little knowledge on the electrochemistry of other metallic materials, including stainless-steel, in organic electrolyte systems. Yashiro *et al.* [15] reported the anodic passivation behavior of typical austenitic stainless-steel, SUS304, in LIB electrolyte containing $LiPF_6$ salt. Fredriksson and Edström [16] have examined so-called duplex stainless steel, LDX 2101, as a possible current collector in LIB system. These research groups demonstrated the surface chemistry of the stainless steel in alkyl carbonate-based electrolyte solutions and its possibility as current-collectors in LIB system. As a result, stainless steel can be used as a possible current-collector for LIB using relatively low operation-voltage cathode and $LiPF_6$-based electrolyte solutions.

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We have also been interested in the use of stainless-steel as a current collector of hybrid capacitor system, where a variety of electrolyte composition could be used [2,17]. In the present work, anodic behavior of austenitic stainless-steel has been investigated in mixed alkyl carbonate-based solutions dissolving different lithium salts, *ie.* $LiPF_6$, $LiBF_4$, $Li(CF_3SO_2)_2N$ (LiTFSA), and $LiClO_4$. Influences of anionic species on the electrochemical stability of stainless steel are discussed in detail.

2. Experimental

The test electrode was a rectangular-shaped SUS304 piece (Nilaco, 8 mm × 20 mm, 0.3 mm thick). The surface of the test electrode was mechanically polished with alumina slurry. And then the working area of 0.8 cm^2 (8 mm ×10 mm) of its one side was provided by sealing the residual part of the test piece with an insulating tape. The working surface was further treated by electro-polishing to obtain smooth surface morphology. A mixed phosphoric/sulfuric acid system (7:3 by volume) at 70 °C (343 K) was used as the polishing bath and current density of 0.2 mA cm^{-2} was applied for 900 s. After the electro-polishing treatment, the test electrode was cleaned by rinsing with distilled de-ionized water and then dried in a vacuum before electrochemical measurements. For comparison, the same size of component metal sheets, Fe (Japan Steel, >99% purity), Ni (Nilaco, 99.9% purity) and Cr (Nilaco, >99% purity), were also used as the test electrode.

A beaker-type three-electrode cell equipped with lithium metal counter and reference electrodes (Li/Li^+) was used for electrochemical experiments. The electrolytic solutions were mixed solvent of ethylene carbonate and dimethyl carbonate (EC + DMC, 1:1 by volume) in which different lithium salts, $LiPF_6$, $LiBF_4$, $Li(CF_3SO_2)_2N$ (LiTFSA), and $LiClO_4$ were respectively dissolved. In some cases, each electrolyte was mixed in a proper mole fraction. The electrolyte concentration was kept 1.0 mol dm^{-3} (M) throughout the work. As all chemicals are Battery Grade, no further purification was done in this work. Water content in the resulting electrolytic solutions was below 20 ppm, except for experiments on the influences of water content in the solution on the electrode behavior. Cyclic voltammetry (CV) using a conventional potentiostat controlled by a personal computer was mainly employed to examine the polarization behavior of SUS304. The potential scan range and the scan rate were between 0.0 and 6.0 V *vs.* Li/Li^+ and 10 mV s^{-1}, respectively. The potential was first scanned from open circuit potential (OCP) to the anodic one, and then turned to cathodic direction at 6.0 V. The potential scan was cycled three times in this potential range. All measurements were conducted at room temperature, 23 ± 2 °C (296 ± 2 K), under a dry Ar atmosphere.

Changes in surface morphology of the stainless-steel electrode were observed by a conventional scanning electron microscope (SEM, Keyence VE8000). After the electrochemical measurements, the test electrode was thoroughly rinsed with DMC solvent and then dried in a vacuum. The sample stage was tilted with 45° to obtain clear images of flat alloy surface, and the working distance (WD) was adjusted according to the surface morphology of each sample. Chemical analysis was also conducted for the electrolyte solutions after the electrochemical measurements. The amount of dissolved metallic species was quantitatively analyzed by an atomic adsorption spectrometer, ICP-AES (Shimadzu, ICPE-9000).

3. Results and Discussion

Fig. 1 shows typical CV responses of stainless-steel SUS304 in EC + DMC solutions containing 1.0 M of lithium salts, $LiPF_6$, $LiBF_4$, LiTFSA, and $LiClO_4$. Although the potential was scanned between 0.0 and 6.0 V vs. Li/Li^+ with 10 mV s^{-1} of the scan rate, here, we will focus on the electrochemical behavior of SUS304 mainly in the potential region above *ca.* 3 V *vs.* Li/Li^+ to discuss the compatibility of the material as the positive electrode current-collector in LIB and LIC systems. In the $LiPF_6$ solution (Fig. 1a), relatively low anodic current was observed at the first scan and much lower currents shown in the following scans. On the other hand, in the $LiBF_4$ solution (Fig. 1b), little bit higher current was observed in the first scan, and its feature of the current response was characteristics to so-called pitting corrosion. That is, since surface layer formed during the anodic potential scan in $LiBF_4$ is less protective with some pits, higher anodic current for metal dissolution still continues through surface pits during the cathodic (backward) potential scan. In both of $LiPF_6$ and $LiBF_4$ solutions, the anodic current was suppressed after the first scan. These observations suggest that the electrode surface was stabilized by the anodic oxidation (passivation) at the first scan in $LiPF_6$ and $LiBF_4$ solutions.

In the solution containing LiTFSA (Fig. 1c), very high anodic current was observed even after the repeated potential cycling. The current responses during the forward (anodic direction) and the reverse (cathodic direction) scans are characteristics to typical pitting corrosion. That is, a partially protective surface layer is formed at 4.5 V (*vs.* Li/Li^+) or above during the forward potential scan, and the anodic oxidation reaction still occurs at 4.0 V or below during the backward potential scan. High anodic current was also observed in the $LiClO_4$ solution (Fig. 1d), where the current hysteresis during the anodic and cathodic scans was much smaller than that observed in the LiTFSA solution.

Fig. 2 shows SEM images of the electrode surface after the above described CV experiments (potential scans of three cycles between 0 - 6 V *vs.* Li/Li^+). The surface of SUS304 after the potential cycling in the $LiPF_6$ solution (Fig. 2a) was very smooth and uniform, suggesting no change even after the potential cycling in the $LiPF_6$ solution. The potential cycling in the $LiBF_4$ solution (Fig. 2b) gave similar surface morphology to the case for $LiPF_6$, but some traces of pitting corrosion were observed in the SEM image of the electrode surface. These results correspond to the CV responses shown in Figs. 1a and 1b.

On the other hand, the surface SEM images of the electrodes after the potential cycling in the LiTFSA and $LiClO_4$ solutions (Figs. 2c and 2d, respectively) were quite different from those observed in the $LiPF_6$ and $LiBF_4$ solutions. Traces of the electrochemical corrosion, or anodic dissolution, were observed for both cases. These surface morphologies seem to correspond to the current profiles observed in the CV experiments (Figs. 1c and 1d). That is, the large current hysteresis observed in LiTFSA (Fig. 1c), suggesting the formation of an insufficiently protective surface layer, provide a partly smooth surface morphology with many pitting traces (Fig. 2c). In the $LiClO_4$ solution, higher anodic current above 4.5 V *vs.* Li/Li^+ with no current hysteresis in the repeated potential cycles (Fig. 1d), corresponding to the continuous dissolution of the electrode, is well consistent with the SEM image shown in Fig. 2d.

Table 1 summarizes the amounts of metal species dissolved in the electrolytic solutions after the CV measurements of SUS304 shown in Fig. 1. In the $LiPF_6$ solution no metal except for Li^+ was observed after the repeated potential cycling. A small amount of Fe was detected after the potential cycling in the $LiBF_4$ solution, although no other cationic species were found in the electrolytic solution. This result reveals that small anodic current observed in the $LiBF_4$ accompanies the anodic dissolution of the alloy component in a very small extent. On the other hand, in the solutions containing LiTFSA and $LiClO_4$, considerable amounts of metallic species were found after the repeated potential cycling between 0 and 6 V *vs.* Li/Li^+. The total amounts of dissolved species were equivalent to coulombic efficiencies of *ca.* 41% and *ca.* 57% in LiTFSA and $LiClO_4$, respectively, when each dissolution reaction is assumed to proceed with three-electron transfer (M = M(III) + 3e; M = Fe, Ni,