Electrochemical Behavior of Graphite Electrode for Lithium Ion Batteries in Mn and Co Additive Electrolytes

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Dissolution of Mn into an electrolyte from $LiMn_2O_4$ in Li ion cell is researched recently. To study an influence of the dissolved manganese species on performance of negative electrode, electrochemical behavior of graphite was investigated in $LiClO_4$ solution containing Mn^{2+} by dissolving $Mn(ClO_4)_2$. During charging, manganese ions were firstly electroreduced on the electrode, followed by Li intercalation into graphite. Mn deposition was confirmed after charge-discharge test, furthermore, the reversible capacity of lithium intercalation was decreased. The results were compared to those in a cobalt additive electrolyte.

Among the candidates of the positive electrode materials for Li ion battery, the $LiMn_2O_4$ system is the most attractive in terms of cost. However, an important problem standing in the way of the wider use of the spinel is its poor storage performance at > 50 ˚C,[1,2] and the general consensus was that the chemical instability of the spinel framework resulting in Mn dissolution was at the origin of the high temperature poor performance. When the manganese species of Mn(II) compounds and/or ions are dissolved from the cathode in a practical cell, the soluble manganese species will be transferred toward an opposite electrode as illustrated in Figure 1a. Manganese ionic species will be easily reduced on the carbon surface because redox potential of Mn/Mn^{2+} is much higher than that of the lithium intercalation into carbon as shown in Figure 1b. In a viewpoint of the influence of dissolved species from cathodes on anodes, the influence of the dissolved manganese species from MnO_2 on Li metal in a primary Li/MnO_2 cell was reported.[3] In the case of secondary lithium-ion or metallic lithium cell, several research groups focused on degradation of the negative electrode.[4,5] Amatucci et al. described that the most obvious would be to have Mn^{2+} reduction on the carbon responsible for the high impedance.[6] For Li ion battery application, a detailed investigation of performance of carbon electrode in a coexistence system of Li^+ and Mn^{2+} ions has not been made yet to our knowledge. Hence, we investigated lithium intercalation into graphite using a graphite/Li half cell with the electrolyte containing lithium and manganese perchlorates. Additionally, since cobalt dissolution from $LiCoO_2$ occurred in a higher potential region,[7] we also discussed the influence of Co^{2+} additive (Figure 1b).

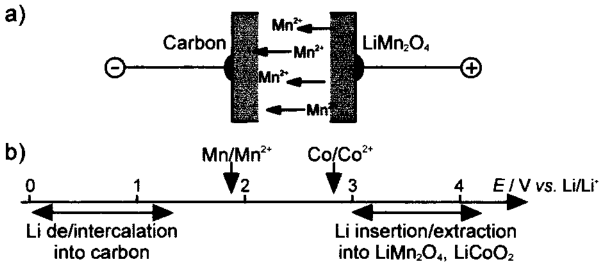

Figure 1. a) Schematic configuration of Li ion battery of $LiMn_2O_4/C$ showing that manganese ions dissolved from positive electrode migrate and diffuse toward negative electrode. b) Potential relation of the battery reactions, such as lithium intercalation into the active materials and standard redox potentials of Mn/Mn^{2+} (1.87 V vs. Li/Li^+) and Co/Co^{2+} (2.77 V vs. Li/Li^+).

Reagent grade graphite (purity 99%, Nakalai Tesque, Inc.), $Mn(ClO_4)_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$ (Aldrich), and $LiClO_4$ (Kanto Chemical Co., Inc.) were used. For preparation of working electrodes, *N*-methylpyrrolidone (NMP) was added to the mixtures of the graphite (about 10 mg) and poly(vinylidene fluoride) as a binder in a mass ratio of 9:1. This mixture was pasted onto Ni net (13 mm in diameter), and then dried at 100 °C to remove the NMP ingredient. After drying, the electrode was pressed and then vacuum dried at 80 °C. Lithium foils were used for both the reference and counter electrodes which were isolated by two glass filters in another compartment filled with an additive-free electrolyte solution in order to avoid deposition of the additives. The electrolyte used was 1 mol dm^{-3} $LiClO_4$ EC + PC (2:1 by volume), containing only trace amount of water less than 20 ppm. Electrochemical investigation was undertaken at 25 ± 2 °C in an Ar atmosphere. A charge–discharge test was carried out between 0.02 and 1.5 V vs Li/Li^+ at 0.1 mA cm^{-2}. Manganese and cobalt perchlorates were used as a source of Mn^{2+} and Co^{2+} additives in order to eliminate the difference of anion species. The hydrates of $Mn(ClO_4)_2{\cdot}6H_2O$ and $Co(ClO_4)_2{\cdot}6H_2O$ were dried at 90–100 °C in vacuum to remove hydrated waters prior to use. Additional water amount in the electrolyte by adding 150 ppm Mn^{2+} and Co^{2+} was less than 90 and 70 ppm, respectively.

The charge-discharge behavior was investigated in electrolyte solutions containing an Mn^{2+} additive as shown in Figure 2. In the Mn-free electrolyte solution, the graphite electrode exhibited high discharge capacity of 340–350 mAh g^{-1}, and the coulombic efficiency (= discharge/charge capacity ratio at each cycle) was relatively high (~ 100 %) except for the first cycle because of the electroreductive formation of solid electrolyte interface (SEI).[8,9] By addition of 40 ppm Mn^{2+}, discharge capacity was decreased somewhat. Furthermore, it was decreased continuously from 320 to 230 mAh g^{-1} in the 150 ppm Mn^{2+}. In case of 150 ppm Mn^{2+}, the graphite electrode showed an initial charge capacity of 1110 mAh g^{-1} from 0.5 V region. It is likely that the too large charge capacity contained the reduction of Mn^{2+} and decomposition of electrolyte on Mn surface followed by lithium intercalation into graphite. SEM and EPMA observations confirmed that the deposited particles on the graphite mainly consisted of manganese. This was direct evidence of deposition of manganese on the surface. It is similar to the results of lithium metal as reported previously.[4,5] Apparently, the reversibility of lithium intercalation was degraded by adding a small quantity of manganese (40 and 150 ppm Mn are equal to 0.72 and 2.7 mmol dm^{-3} $Mn(ClO_4)_2$, respectively). In a practical cell, concentration of dissolved manganese will become higher of several hun-

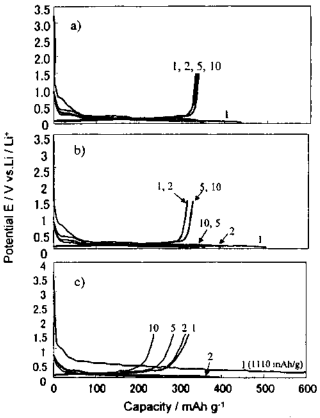

Figure 2. Charge-discharge curves of graphite electrodes at 0.1 mA cm^{-2} in 1 mol dm^{-3} LiClO$_4$ EC/PC (2:1) containing a) 0 (Mn^{2+}-free), b) 40, and c) 150 ppm Mn^{2+} additive.

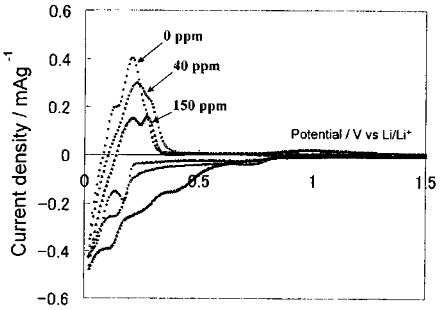

Figure 3. Cyclic voltammograms of graphite electrodes at 0.1 mV s^{-1} in 1 mol dm^{-3} LiClO$_4$ EC/PC (2:1) containing 0 - 150 ppm Mn^{2+} electrolyte.

dreds ppm because of small volume of electrolyte solution. Hence, this degradation will arise more severely in a practical cell.

Figure 3 compares cyclic voltammograms of graphite electrode at the first cycle. In the first cathodic scan, higher reductive currents flow between 1.0 and 0.1 V in the Mn^{2+} containing solutions. Simultaneously reversible current in the anodic scan was decreased remarkably. As described previously,[10] the intercalation of Mn^{2+} ions hardly occurred into the graphite. Hence, we concluded that this reduction was predominantly due to electrochemical deposition of metallic manganese. By assuming that activity of ion is equal to concentration in the EC/PC, practical redox potentials of Mn/(150 ppm Mn^{2+}) is estimated as 1.79 V vs Li/Li$^+$. After the electrodeposition of manganese, the decomposition of solvent, i.e., the formation of an SEI layer, must occur on the surface of manganese metal. It is likely that the Mn metal and/or manganese compounds on the graphite showed high (electro-)chemical reactivity, and decomposition of electrolyte, which was independent on the formation of SEI, was promoted on the Mn surface. By successive cycling, the electrode was covered with the decomposition products, which would be an origin of the high impedance.[6] From Figures 2c and 3, discharge (anodic) current was observed from 0.4 to 1.5 V which would be due to dissolution of remaining active Mn metal.

Figure 4 shows the charge–discharge curves in Co^{2+} added electrolytes. By adding 40 ppm Co^{2+}, the graphite exhibited lower discharge capacity of ca. 300 mAh g^{-1} with low coulombic efficiency. In case of 150 ppm Co^{2+}, the initial charge occurred from 1.6 V region, and its capacity of 1770 mAh g^{-1} was higher than that of 150 ppm Mn^{2+}. It was likely that the charge capacity, which is about five times as high as the theoretical capacity of LiC$_6$, was not due to electrochemical intercalation of Co^{2+} but to electrodeposition of cobalt metal. Furthermore, electrochemical decomposition of electrolyte and/or Li$_n$Co alloying may be promoted by the Co metal on the graphite. Addition of 150 ppm Co^{2+} makes the coulombic efficiency quite low during initial few cycles, and then discharge capacity and the coulombic efficiency were gradually improved. After 10 cycles, the discharge capacity became higher than that of 0 ppm (see Figure 2a) with high coulombic efficiency of 90%. As can be seen in Figure 4b, the capacity of lithium deintercalation below ca. 0.3 V increased from 180 to 270 mAh g^{-1} followed by constant discharge capacity of about 80 mAh g^{-1} in the region of 0.3–1.5 V. The capacity in the higher potential region probably corresponds to Li dissolution from Li$_n$Co alloy and/or partial dissolution of the Co metal. This improvement of reversibility of lithium intercalation presumably resulted from reducing the electrode resistance. Similarly, depositing silver particles onto graphite anode improved the discharge capacity because of decrease in electrical resistance of the electrode as reported previously.[11] In a practical LiCoO$_2$/C cell, when cobalt dissolution occurs by overcharging, the influence on negative graphite electrode is expected to be gradually diminished by the following several cycles.

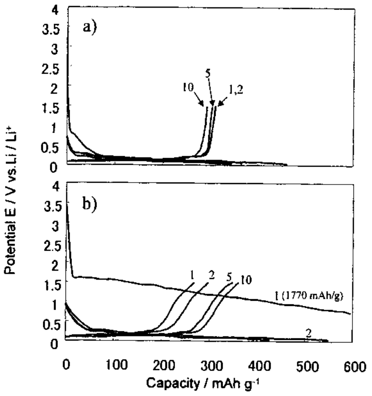

Figure 4. Charge-discharge curves of graphite electrodes at 0.1 mA cm^{-2} in 1 mol dm^{-3} LiClO$_4$ EC/PC (2:1) containing a) 40 and b) 150 ppm Co^{2+} additive.

References and Notes

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