

Effects of Metal Ions Addition on Carbon Anode Performance for Lithium-ion Batteries

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Since manganese dissolution from the spinel LiMn_2O_4 in the lithium ion cell was reported, some mechanisms of the Mn dissolution and its suppression methods were studied by Oh's [1], Tarascon's [2], and Yoshio's groups [3]. In a practical cell, the soluble manganese species will reach the carbon anode. Hence, manganese ionic species will be reduced on the carbon readily because the standard potential of Mn/Mn^{2+} (ca. 1.8 V vs. Li/Li^+) is much higher than that of the lithium intercalation into graphite [4]. Amatucci *et al.* described that the most obvious would be to have Mn^{2+} reduction (Mn plating) on the carbon responsible for the large impedance of the anode surface [5]. To analyze and clarify this, we recently reported the influence of the dissolved Mn(II) and Co(II) additives in an electrolyte solution on lithium intercalation into carbon anode [4]. In this study, furthermore, we investigated graphite anode performance in the electrolytes containing various metal perchlorates or iodides.

Metal ion additives used were soluble perchlorates of Mg(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), and Pb(II), and iodides of Li(I), Al(III), and Sn(II). Hydrates of some additives were dried at high temperature in vacuum prior to use. These were added in 1 mol dm^{-3} LiClO_4 EC + DEC (1:1) or EC + PC (2:1). Graphite/PVDF was used as working electrode. Lithium foils were used for both the reference and counter electrodes which were isolated by two glass filters in another compartment [4]. Electrochemical investigation was undertaken at 25°C. Charge-discharge test was carried out between 0.02 ~ 1.5 V vs. Li/Li^+ at 0.1 mA cm^{-2} .

The influences on the anode performance were quite different among the kinds of metallic ions. The reversible lithium intercalation into a graphite anode was degraded by the 40 ~ 150 ppm Mn(II) addition, that is, discharge capacities of the carbon were decreased with increasing the amount of Mn(II). From the voltammetry and elemental analysis, we confirmed that manganese deposition (not intercalation) firstly occurred on the carbon during the initial charge followed by SEI formation and lithium intercalation. On the surface of deposited metallic Mn particles, electrolyte decomposition would be much electrocatalyzed, which was confirmed by the voltammetry of a manganese metal electrode. It means that remarkable degradation occurs for a practical C/ LiMn_2O_4 cell because of the low coulombic efficiency of the anode. When the same amount of Mn(II) was added in the additive free electrolyte between 5th discharge/6th charge, the degree of decreasing the discharge capacities became smaller because of the existence of alternative SEI.

When iodide ions was added using LiI, the efficiency and reversible capacity were improved. Further, the influence of Mn(II) was suppressed by adding LiI before cycling. It is likely that iodide ions was suppressed the electrolyte decomposition by adsorbing on the Mn surface.

In cases of adding Mg(II), Ni(II), Cu(II), and Sn(II) in the electrolyte, reversibility of the graphite was degraded since the additives were deposited during the initial charge. The electrode was covered with the deposits which hindered lithium intercalation and/or accelerated decomposition of the electrolyte. On the other hand, by adding Co(II), Zn(II), Ag(I), and Pb(II), and Al(III) before cycling, reversible capacities of the anode increased over the theoretical capacity of graphite, 372 mAh g^{-1} , since the alloy of Zn-Li, Ag-Li, Pb-Li and Al-Li was effectively formed with the deposited metals. For Co(II) addition, the increase of capacity might be due to nano-sized deposits of Co although no 3d metals form alloys with Li [7].

References

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