

2-Vinylpyridine as Film-forming Additive to Suppress the Degradation of Carbon Anode by Dissolved Manganese for C/LiMn₂O₄ Rechargeable Battery

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For lithium-ion batteries of C/(spinel Li–Mn–O), the sever capacity loss occurs after storage of the battery at >50 °C. This is mainly due to degradation of the carbon which was induced by electroreduction of Mn(II) dissolved from the spinel; this step is followed by the irreversible electrochemical reaction at the graphite/(Mn deposits)/electrolyte interface. However, 2-vinylpyridine as an additive into the electrolyte was capable of suppressing this degradation of graphite anode, therefore, improved the battery performances. During the first charge, electropolymerization of 2-vinylpyridine from about 0.9 V vs Li⁺ resulted in film formation of poly(2-vinylpyridine) on the anode surface. The polymer protected the graphite from dissolved Mn(II).

Manganese dissolution from the spinel occurs by high temperature storage of the C/LiMn₂O₄ battery at >50 °C and leads to degradation of the carbon anode. Some chemical mechanisms of the Mn dissolution as well as methods to suppress it were addressed by some groups.^{1–4} Recently, we emphasized that the soluble manganese species diffuse through the electrolyte to reach the carbon anode; then, manganese is readily deposited on the carbon. We concluded that the deposition induced the degradation on the anode side.⁵ No manganese dissolution from the spinel would be still difficult to solve the degradation problem of the C/(spinel Li–Mn–O) cell to our knowledge. Therefore, a protection of the negative electrode from soluble Mn(II) is important for enhancement of large sized C/LiMn₂O₄ batteries for vehicle power sources. On the other hand, electropolymerization is one of the most interesting and simplest techniques for fabricating polymer-modified electrode.⁶ We believe that vinyl-type polymers synthesized by electroreduction^{7,8} are advantageous to direct film formation on a negative electrode. In this study, we investigated the graphite anode performance in electrolytes containing small amount of a new additive, 2-vinylpyridine (VP), in order to suppress the degradation caused by Mn(II) reduction, and compared to that for vinylene carbonate (VC).⁹

Reagent grade natural graphite (Nakalai Tesque, Inc., average particle size 10 μ m), manganese(II) perchlorate, 2-vinylpyridine, and vinylene carbonate were used. Details of the electrochemical measurement are described in our previous paper.⁵ Mixture of the graphite (from 10 to 20 mg) and poly(vinylidene fluoride) in a weight ratio of 9 : 1 was used for preparation of working electrodes. Li foils were used for both the reference and counter electrodes. Charge-discharge (lithium intercalation-deintercalation, respectively) tests were carried out between 0.02 and 1.5 V vs Li/Li⁺ at 0.1 mA cm⁻² and 25 \pm 2 °C in Ar. The electrolyte used was 1 mol dm⁻³ LiClO₄ EC-DEC

(1 : 1 by volume). VP (14, 0.7 and 0.14% by volume) was dissolved into the electrolyte prior to battery tests. Soluble Mn(II) perchlorate (150 ppm Mn(II)) was added after the 5th discharge.

Figure 1 shows the initial charge-discharge curves in electrolytes with various amounts of VP. For VP free (Figure 1d), the natural graphite shows a reversible capacity of 344 mA h g⁻¹, and an irreversible capacity of ca. 90 mA h g⁻¹ was observed at the first, which is well known to be due to the electroreductive formation of the solid electrolyte interface (SEI) on graphite around 0.8–0.3 V. In VP-added electrolytes, the additional plateau appears clearly around 0.9 V in the curve, and SEM observation confirmed deposits on the electrode. It is most likely that this is due to the electroreductive polymerization of VP as shown in Scheme 1 in consideration of previous literature;^{7,8} the formation of poly(2-vinylpyridine) film.

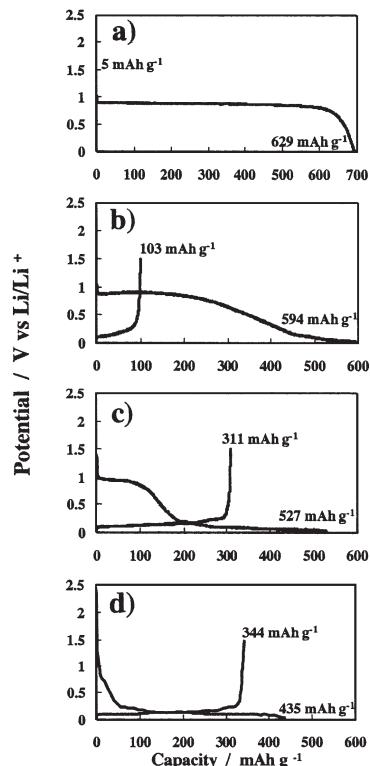
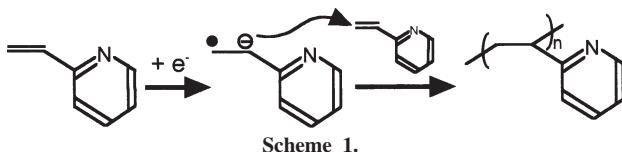


Figure 1. Initial charge-discharge curves of graphite electrodes at 0.1 mA cm⁻² in LiClO₄ EC/DEC (1 : 1) with a) 14, b) 0.7, c) 0.14% VP additive, and d) no additive.

This electroreductive polymerization brought about the in situ polymer coating on the graphite during the initial charge. The quantity of charge passed at the plateau increased with the



increase of VP concentration. It is thought that the thickness of the polymer also increased for the higher concentration of VP. In case of larger amount of the deposits, the potential plateau around 0 V for lithium intercalation into graphite decreased, and it finally disappeared because thicker polymer film interfered lithium intercalation into graphite. As a result, the discharge (deintercalation) capacity also decreased. However, the discharge capacity was relatively higher only for lower concentration, 0.14% VP.

When the Mn dissolution occurs in the practical cell after several cycles, the graphite electrode is already modified with SEI. So, manganese perchlorate (150 ppm Mn(II)) where the degradation of battery performance was clearly observed⁵ was added after the fifth discharge, and the charge-discharge cycling behaviors were compared in electrolytes with and without VP (0.14%) as illustrated in Figure 2. At the sixth, the charge capacity became pretty large of 1680 mA h g⁻¹ with huge irreversibility because of the electroreduction of Mn(II) and the decomposition as described previously;⁵ nevertheless, the VP addition successfully suppressed the irreversible reactions, and the capacity retention was also improved after the fifth cycle.

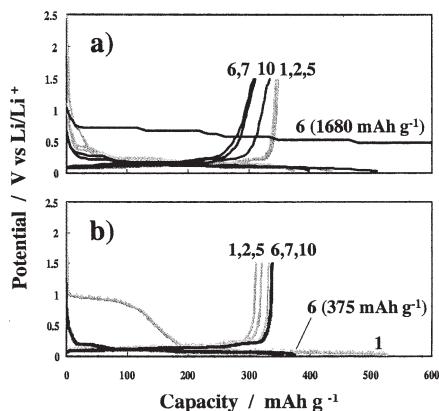


Figure 2. Charge-discharge curves of graphite electrodes at 0.1 mA cm⁻² in LiClO₄ EC/DEC (1 : 1) with a) no additive and b) 0.14% VP. Manganese(II) perchlorate ([Mn] = 150 ppm) was added before the sixth charge.

Figure 3 shows variations in the discharge capacity and coulombic efficiency (defined as a ratio of discharge to charge capacities at each cycle). In the case of VP free, the coulombic efficiency at the six cycle dramatically reduced to 20% which is due to the dissolved Mn(II). One can understand that this lower efficiency leads to severe capacity loss of a practical C/LiMn₂O₄ cell considering the absolute capacity balance of negative/positive electrodes, even though the capacity was recovered in the following cycle.⁵ Therefore, not only the discharge capacity but the efficiency of a graphite anode should be improved even after 150 ppm Mn(II) addition. For the VP added system, the efficiency at the sixth was much improved, furthermore, the discharge curves and capacities were hardly changed after Mn(II) addition as shown in Figures 2 and 3. From characteristic X-ray analysis of the tested electrode, the peak intensity of manganese

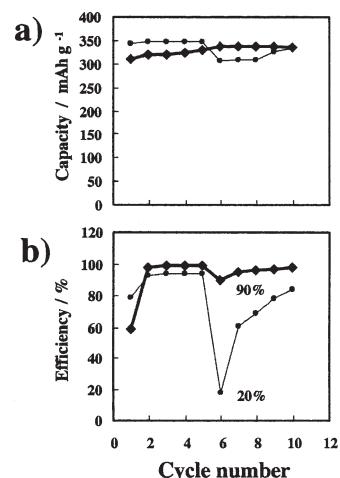


Figure 3. Comparison of a) discharge capacities and b) coulombic efficiencies of graphite electrodes at 0.1 mA cm⁻² in LiClO₄ EC/DEC (1 : 1) without (thin line) and with 0.14% VP (thick line). Manganese(II) perchlorate ([Mn] = 150 ppm) was added before the sixth charge.

became lower for the VP added electrolyte. We believe that film-forming VP was effective to suppress the Mn deposition, namely, it depressed the irreversible reactions at the carbon. On the other hand, VC additive which has a polymerizable double bond comparable to VP is known to be positive to improve the performance of the graphite.^{9,10} However, it (6.6 vol% VC) hardly eliminated the Mn(II) degradation in our conditions. There is general agreement that the SEI surface film formed on the carbon anode consists of a heterogeneous mixture of inorganic/organic compounds dependent on electrolyte additives. It is likely that the functionality of the surface film formed in the VC system differs from that of the VP. Consequently, novel types of additives are essentially important and necessary for the suppression of the deterioration, and the further analyses and development of such kinds of additive are now in progress in order to enhance the C/LiMn₂O₄ battery system.

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