

Is LiPF₆ a Suitable Salt for the Study on Reduction Reaction in Nonaqueous Solutions?

비수용액의 환원반응연구에 있어서 LiPF₆는 적합한 염인가?

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This study reports the passive nature of lithium ion battery electrolytes containing LiPF₆ as a salt. Two reduction peaks are invariably present between 2.8 and 1.2 V (vs. Li⁺/Li) in the cyclic voltammogram using a Pt electrode in LiPF₆ solutions irrespective of the kind of solvents. The reduction peaks disappear at the second cycle (Fig. 1). The reduction reaction is enhanced if the solution is exposed to elevated temperature or water contamination, while it is absent in the solutions containing Li salts other than LiPF₆ such as LiBF₄, LiBOB, and LiBeti. The reduction reaction is found to be due to the trace amount of HF that is inevitably present in LiPF₆ solutions (Fig. 2). Based on the Rotating Ring Disk Electrode experiment, two reduction peaks are ascribed to two successive reactions; reductive proton adsorption and evolution of molecular H₂ on Pt surface. The reduction of HF passivates Pt surface probably forming LiF, which suppresses the reduction reactions of other electrolyte components otherwise occurred below 2.8 V. For example, electrodeposition of Mn, which takes place below 1.5 V in LiBF₄ or LiBeti solutions, is severely hampered in LiPF₆ solution.

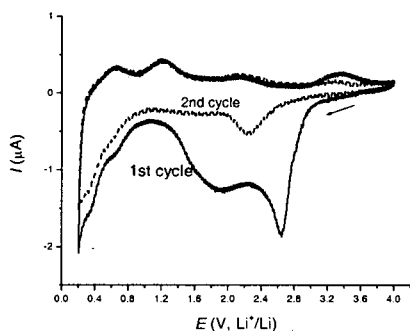


Fig. 1. Two consecutive cycles of cyclic voltammogram for 1M LiPF₆ in EC/EMC (1/2, v/v). Two reduction peaks are shown between 2.8 and 1.2V at the first cathodic scan. These peaks are absent at the second scan.

Working : Pt, Reference : Li, and Counter : Pt. Scan rate : 10mV/s. Ar atmosphere (H₂O and O₂ < 5ppm). 27±2°C.

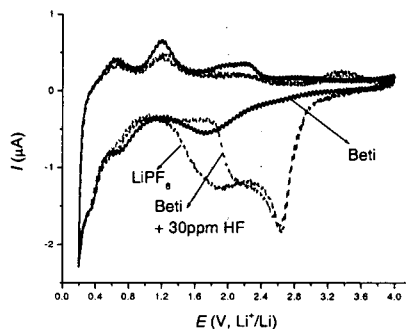


Fig. 2. Comparison of the first cycles in EC/EMC (1/2, v/v) containing 1 M LiPF₆, 1 M LiBeti, and 1M LiBeti with 30 ppm HF. For LiBeti solution, the reduction peaks observed for LiPF₆ are absent. When 30 ppm HF is added into LiBeti solution, the reduction peaks are shown.