HIGHLY CONCENTRATED ELECTROLYTES FOR 5-V CATHODES

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Highly concentrated electrolytes have many unique properties,[1-4] such as Li^+-intercalation into graphite anode without EC,[1,3] suppression of S_8^{2-} ion dissolution in Li-S batteries, etc., and is attracting much attention of many researchers. In highly concentrated electrolytes, all solvent molecules are strongly coordinated with Li^+ ions, and hence the stability of the electrolytes against oxidation is improved significantly. Yoshida et al. reported that $LiCoO_2$, which is a 4-V cathode, can be charged and discharged in a LiTFSI/triglyme (1:1) electrolyte with good cycleability,[3] though triglyme is an ether compound and usually cannot be used as solvent.
5-V cathodes, e.g. $LiNi_{0.5}Mn_{1.5}O_4$ and $LiCoPO_4$, are promising for the next-generation LIBs with high energy densities. Unfortunately no electrolyte systems that tolerate the highly oxidative 5 V cathode have been reported so far. In the present study, we investigated the effect of concentration on the stability of highly concentrated electrolytes, $LiPF_6$/PC and $LiBF_4$/PC, against a 5-V cathode, $LiNi_{0.5}Mn_{1.5}O_4$ to realize 5-V LIBs with high energy densities.

Figure 1 compares charge/discharge curves of a 5-V spinel $LiNi_{0.5}Mn_{1.5}O_4$ in standard (0.83 mol kg-1, 1 M, Li/PC = 11.8) and highly concentrated (4.9 mol kg^{-1}, Li/PC = 2) $LiBF_4$/PC at 30°C. The charge/discharge rate of C/10 was employed to emphasize electrolyte decomposition. Thought the $LiNi_{0.5}Mn_{1.5}O_4$ can be charged and discharged in both electrolytes, the irreversible capacity (Q_{irr}) in 1 M $LiBF_4$/PC was high (76 mAh g^{-1}) because of vigorous electrolyte decomposition. In contrast, Q_{irr} was significantly reduced in the concentrated electrolyte, which indicated that stability against oxidation was improved in the highly concentrated electrolyte. Similar tendency was also observed in highly concentrated $LiPF_6$/PC electrolytes, though polarization on charging and discharging were much higher.

A fresh half-cell was fully charged to 5.0 V, and kept at 60°C for 3 days in $LiPF_6$/PC electrolytes. The amount of Mn deposited on lithium counter electrode was evaluated by ICP as a measure of dissolved Mn ions. The amount of dissolved Mn ions decreased with increasing Li/PC ratio, which indicated that the use of highly concentrated electrolytes is also effective for suppressing Mn ion dissolution.

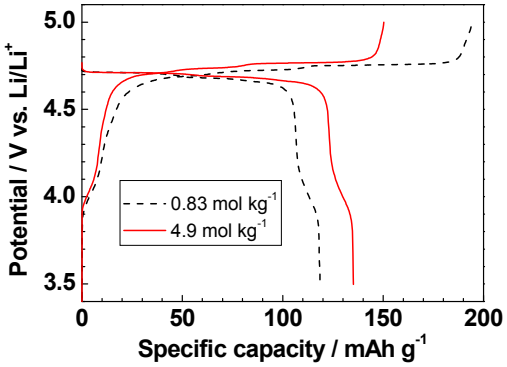

Fig. 1 Charge and discharge curves of $LiNi_{0.5}Mn_{1.5}O_4$ in 0.83 mol kg^{-1} (1 M) and 4.9 mol kg^{-1} $LiBF_4$/PC at 30°C. Charge and discharge rate: C/10.

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References: [1] S.-K. Jeong et al., J. Power Sources, 175, 540 (2008).; [2] K. Dokko, et al., J. Electrochem. Soc., 160, A1304 (2013).; [3] K. Yoshida, et al., J. Am. Chem. Soc., 133,13121 (2011).; [4] Y. Yamada, et al., ACS Appl. Mater. Interfaces, 6, 10892 (2014).