

Effect of Titanium Substitution on the Compatibility of Electrodes with Pyrrolidinium-Based Ionic Liquid Electrolytes

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The quest for the development of rechargeable lithium-metal batteries has attracted vigorous worldwide research efforts because this system offers the highest theoretical specific energy [1]. For this to be achieved, the repetitive deposition and stripping of lithium must be close to fully reversible. Thus, alternative electrolytes have been investigated, such as the room-temperature ionic liquid (RTILs). Lithium can be cycled with a high degree of reversibility with efficiencies exceeding 99% using systems based on N-methyl N-alkyl pyrrolidinium (P_{1X}^+) combined with the TFSI anion [2]. More recent efforts have been directed towards systems based on P_{1X}^+ cations with the FSI anion and appear to be even more promising [3,4]. In this work, we discuss to what extent RTILs based on P_{1X}^+ cations with TFSI or FSI anions can be used as electrolytes for rechargeable Li batteries. In particular, their physical and chemical properties are thoroughly discussed so as to explain the difference observed in their electrochemical behaviour. Although these two systems seem to be stable against lithium, their compatibilities with cathode materials require full assessment as well. Thus, various manganese oxide cathodes are investigated in this study. Strategies to minimize cathode dissolution are also debated, such as the substitution of part of the manganese for titanium [Figure 1].

References:

- [1] J. M. Tarascon, M. Armand, *Nature*, **414** (2001) 359
- [2] P. C. Howlett, D. R. MacFarlane, A. F. Hollenkamp, *Electrochem. Solid-State Lett.*, **7** (2004) 97
- [3] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kibuta, E. Ishiko, M. Kono, *J. Power Sources*, **160** (2006) 1308
- [4] M. Ishikawa, T. Sugimoto, M. Kibuta, E. Ishiko, M. Kono, *J. Power Sources*, **162** (2006) 658

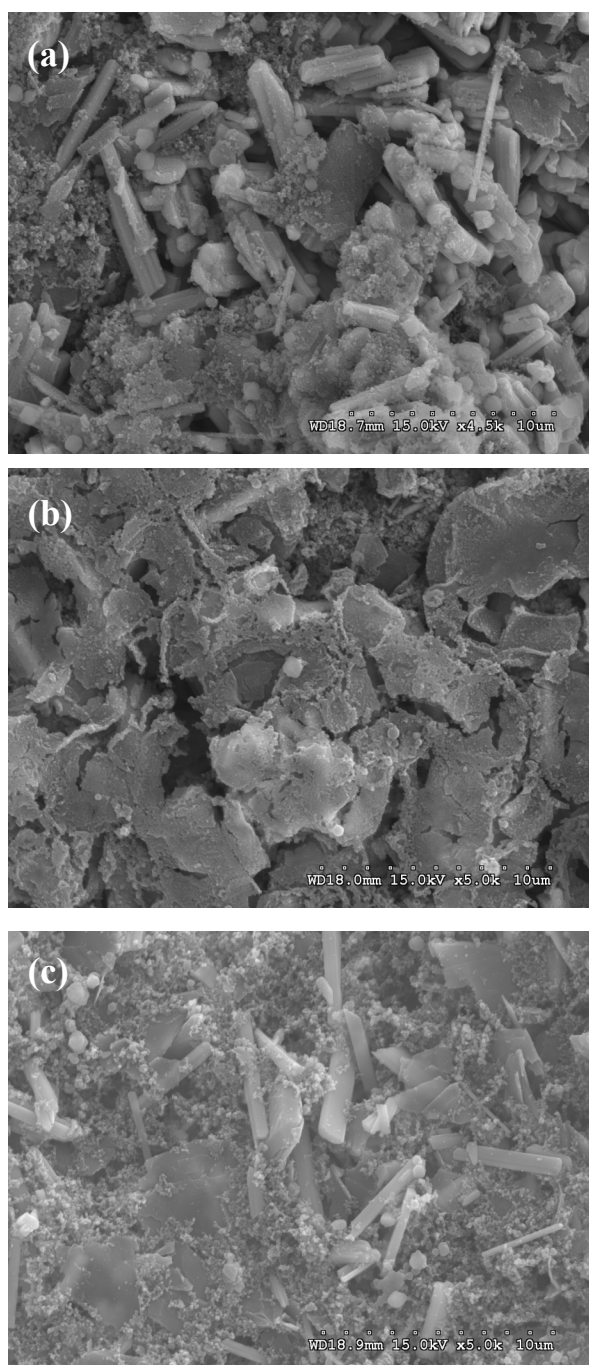


Figure 1: SEM micrographs of cycled manganese oxides cathodes : (a) Li_xMnO_2 in EC:DMC (1:2), 1M LiPF6 (450h), (b) Li_xMnO_2 in $P_{13}TFSI$, 0.5M LiTFSI (450h), (c) $Li_xTi_{0.11}Mn_{0.89}O_2$ in $P_{13}TFSI$, 0.5M LiTFSI (450h)