

Fluorosilane-Based Electrolyte Additives
to Improve High Temperature Performance
of Graphite/LiMn₂O₄ Li-Ion Cells

S. Komaba,^a D. Morita,^a N. Yabuuchi,^a K. Yamagiwa,^a M. Taki,^b T. Otsuka,^b T. Yano,^b J.-Y. Son,^c Y.-T. Cui,^c and H. Oji^c

^aDepartment of Applied Chemistry, Tokyo Univ. of Science, Shinjuku, Tokyo 162-8601, Japan

^bADEKA Corporation, Arakawa, Tokyo 116-8553, Japan

^cJapan Synchrotron Radiation Research Institute/SPRING-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan

Since the first commercialization in 1991, technology of lithium-ion batteries is now highly sophisticated as power sources for mobile electronics applications. Spinel-type LiMn₂O₄-based electrode materials have recently attracted interest as cost-effective electrode materials, especially for electric vehicles. Dissolution of manganese ions, especially at elevated temperatures, is known to be a disadvantage of LiMn₂O₄-based electrode materials. Dissolved manganese ions are electrochemically reduced and deposited at the surface of graphite electrodes, presumably as metallic manganese. Severe electrolyte decomposition on the surface of deposited metallic manganese, resulting in formation of oxides and/or organic compounds containing manganese, deteriorates the electrode performance of the graphite negative electrodes [1]. Among various film-forming electrolyte additives to improve battery performance, 2-vinylpyridine is found to be an efficient additive to overcome the issue associated with the dissolution of manganese ions from LiMn₂O₄ [2]. Electrochemical reduction of the electrolyte additives induces the formation of surface film at the graphite electrode. Herein, we report new effective electrolyte additives for graphite/LiMn₂O₄ cells, i.e., fluorosilane-based organic compound (Figure 1).

The fluorosilane-based additives suppress the self-discharge of LiMn₂O₄ during 60°C storage associated with the formation of surface film at the surface of LiMn₂O₄. Figure 2 compares charge/discharge curves of graphite/LiMn₂O₄ cells with or without the fluorosilane-based electrolyte additive. Stoichiometric and nanosized (~100 nm) LiMn₂O₄ is utilized in this study to accelerate the degradation as positive electrodes. After 10 cycles at room temperature, the fully charged cells were stored at 60°C for 7 days, and then tested at room temperature. Reversible capacity is significantly reduced by the storage at elevated temperatures when the electrolyte additive is not used. However, the capacity reduction is successfully suppressed by the additive in Fig. 2. To examine the origin of improved performance by storage at 60°C with the fluorosilane-based additive, photoelectron spectroscopy (PES) was utilized. Both hard (7939 eV) and soft (1480 eV) X-ray radiation is utilized for PES to study the surface film with different detection depth. Hard X-ray PES (HAXPES) allows us to analyze deeper region (~10 nm) compared with soft X-ray PES (SXPES) (~few nm). Figure 3 compares PES spectra for the LiMn₂O₄ electrodes stored at 60°C for 7 days with or without additives. PES studies confirm that a Si-containing thicker surface layer exists on the LiMn₂O₄ electrode when the fluorosilane-based additive is utilized. The Si-containing surface layer is expected to be suppressed the self-

discharge at elevated temperatures. From these results, we will further discuss improved mechanisms for the performance of graphite/LiMn₂O₄ cells and corresponding half Li cells with the fluorosilane-based additives.

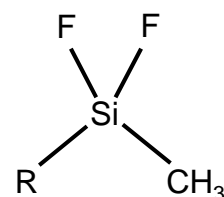


Figure 1. A structural formula of a fluorosilane-based electrolyte additive used in this study.

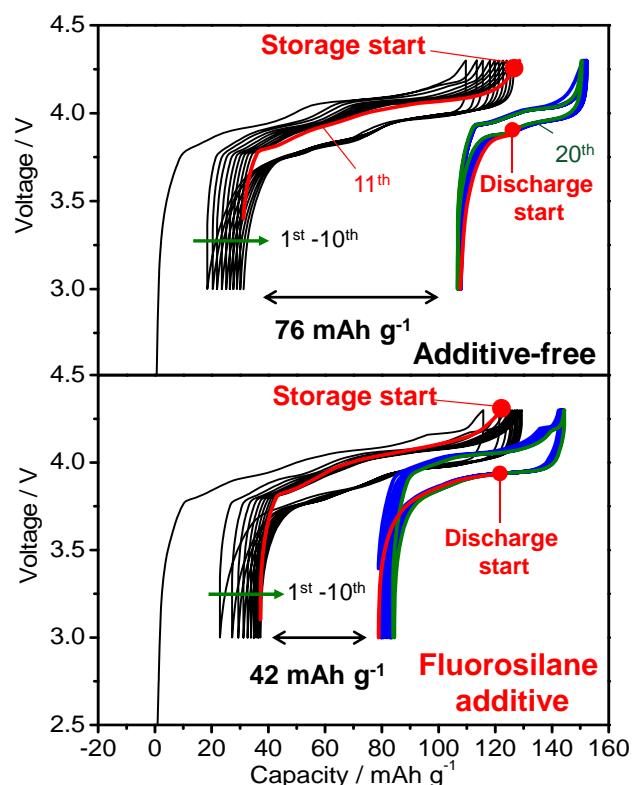


Figure 2. A comparison of charge/discharge curves of graphite/LiMn₂O₄ cells tested at room temperature before (black lines) and after (blue lines) the storage at 60°C for 7 days with or without the fluorosilane-based additive.

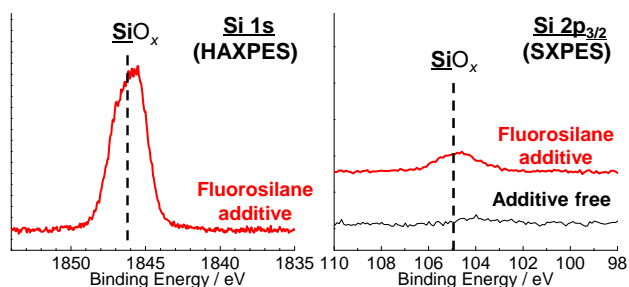


Figure 3. Si 1s hard and Si 2p_{3/2} soft X-ray photoelectron spectra of LiMn₂O₄ electrodes after the 60°C storage test with the fluorosilane-based electrolyte additive.

References

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Acknowledgements

This study was partly supported by the NEXT program from the Japanese Ministry of MEXT.