Artificially-built passivating film on $LiNi_{0.5}Mn_{1.5}O_4$ by molecular layer deposition of (pentafluorophenylpropyl)trimethoxysilane

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1. Introduction

The manganese spinel ($LiNi_{0.5}Mn_{1.5}O_4$, LNMO) is a promising high-voltage (~4.7 V *vs*. Li/Li^+) positive electrode for lithium-ion batteries (LIBs). However, since the working voltage is far beyond the electrochemical stability window of common electrolytes (~4.3 V), electrolyte decomposes during cycling and surface film deposits. This irreversible reaction lowers Coulombic efficiency. The surface film growth brings out large polarization and leads to capacity fading. Moreover, acid that is generated as a result of electrolyte decomposition etches the LNMO electrodes and accelerates film growth. In this work, (pentafluorophenylpropyl)trimethoxysilane (PFPPS) is selected as a film-forming precursor to generate passivating film on the surface of LNMO. The cycle performance of LNMO electrodes is significantly improved as the result of surface modification.

2. Experimental

The PFPPS-grafted LNMO was prepared by molecular layer deposition (MLD) to provide dense and uniform coating. Surface characterization was performed by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The galvanostatic charge/discharge cycling of Li/LNMO cell was performed at 25°C and 60°C, respectively. Meanwhile, the degree of film growth and subsequent film resistance after cycling were compared by XPS, SEM and AC impedance tests.

3. Results and discussion

The PFPPS-grafted LNMO outperforms the pristine (non-treated) LNMO. The PFPPS-derived surface layer does not suffer from oxidation until 4.9 V. Moreover, the PFPPS layer effectively passivates the LNMO surface from the oxidative electrolyte decomposition to give higher Coulombic efficiency. Consequently, the surface film growth and cell polarization are less severe to allow better capacity retention for Li/LNMO cells.

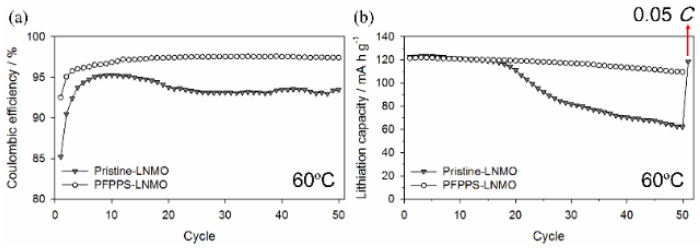

Figure 1. (a) Coulombic efficiency and (b) cycle performance of Li/LNMO cells at 60°C