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A facile method for construction of a functionalized multi-layered separator to enhance cycle performance of lithium manganese oxide†

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A facile approach has been proposed to improve the cycle performance of $LiMn_2O_4$-based cathodes by chemical modification of the separator. This strategy is based on the construction of a multilayer structure consisting of an interlayer with polar hydroxyl (OH) groups to promote the chemical reactivity between a hydrophobic separator and a surface layer with a HF scavenger to remove any HF remaining in the electrolyte. Systematic studies performed in this work indicate that separator functionalization is effective in increasing the structural stability of $LiMn_2O_4$ cathodes.

Recently, lithium manganese oxide ($LiMn_2O_4$) has emerged as a promising cathode material with the potential to replace commercial lithium cobalt oxide ($LiCoO_2$), owing to its low cost, natural abundance, low toxicity, good safety characteristics, and high power density.[1–5] Despite these advantages, $LiMn_2O_4$ still lacks commercial implementation because of insufficient cycle performance arising from structural instability, especially at elevated temperatures. The instability of $LiMn_2O_4$ is mainly caused by the accelerated dissolution of Mn ions in the presence of hydrofluoric acid (HF) produced by the reaction between $LiPF_6$ and H_2O in the electrolyte, resulting in irreversible decomposition of $LiMn_2O_4$ to MnO, MnO_2, and MnF_2 by reacting with HF.[6–8] In addition, Mn ions dissolved in the electrolyte readily form reduced Mn particles on the anode surface, which hinder the formation of stable solid electrolyte interfaces (SEIs) and it significantly affects the cycle performance of the cathode in lithium ion batteries (LIBs).[9–12] Therefore, there is a critical need for strategies to prevent the dissolution of Mn ions in the electrolyte in order to enhance the cycle performance of $LiMn_2O_4$-based LIBs. Thus far, to prevent the dissolution of Mn ions from $LiMn_2O_4$-based cathodes, researchers have attempted to improve the structural stability of the cathodes at elevated temperatures. The two most frequently used approaches that essentially focus on cathode modification[13–17] and utilization of additives in the electrolyte, which chemically scavenge the HF formed in the electrolyte.[18–20] However, to the best of our knowledge, there are no reports so far in the literature that deal with separator modification as a possible approach for preventing the dissolution of Mn ions. To this end, we propose a novel approach of separator modification by a HF scavenging layer for improving the electrochemical performance of $LiMn_2O_4$-based cathodes employed in LIBs. In contrast to conventional cathode and electrolyte modification techniques, the separator modification approach proposed in this study is novel and has not been attempted before.

Among the candidates for HF scavenging, tetraethylorthosilicate (TEOS) has been shown to be effective in enhancing cycle performance of $LiMn_2O_4$-based cathodes owing to their desirable chemical structure: TEOS provides significantly more reaction sites to remove HF (there are three reaction sites in one mole of TEOS) through the reaction of F^- and Si.[21,22] However, direct installation of a TEOS layer on a polyethylene (PE) separator is unattainable owing to the lack of chemical functionalities of PE separators as they are composed of chemically stable olefin ($-CH_2CH_2-$) units. Therefore, an interlayer with specific functionality (which enables its components to react with TEOS) is required to install the TEOS layer on the separator surface. In this regard, alcohol functionality is highly desirable for the interlayer component: the polar hydroxyl (OH) group readily reacts with TEOS *via* an alcohol–ester condensation reaction.[23–25] Among the many candidates for the interlayer, SiO_2 is one of the more attractive components: it has a sufficient number of polar hydroxyl (OH) groups during the synthesis process to advance the reaction rate of the interlayer and TEOS. Additionally, from the viewpoint of chemical reactivity, the condensation reaction between the OH group and orthosilicate has many advantages such as low reaction temperature, high processability, and eco-friendliness. With this synthetic strategy, a novel multi-layered functional separator has been

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developed to prevent dissolution of Mn ions and improve the cycle performance of $LiMn_2O_4$-based cathodes.

Fig. 1 illustrates the synthetic scheme of the modified separator proposed in this study. For the facile chemical modification of the hydrophobic separator, an alcohol-functionalized interlayer was introduced by dip coating the PE separator with the SiO_2. Furthermore, an additional HF scavenging layer was successfully introduced by chemical treatment *via* a simple alcohol–ester condensation reaction (detailed experimental procedure and mechanism for alcohol–ester condensation are presented in ESI†). The SEM analysis (Fig. 2a and b) revealed that the morphology of the separator was quite different: contrary to the bare PE, a uniformly covered layer was clearly observed on the surface of the PE–SiO_2–TEOS separator. The components of the modified layer were characterized by energy dispersive spectroscopy (EDS) analysis: they contained 13.7 wt% of Si derived from TEOS as a result of the chemical reaction with OH in an interlayer. The elemental mapping results also confirmed the presence of a finely dispersed TEOS layer: the main elements of the outer layer (Si and O) completely covered the surface of the modified separator, as shown in Fig. 2c. This is in good agreement with results of the wettability tests using polar electrolytes (Fig. S2†): the PE–SiO_2–TEOS separator was more compatible with polar electrolytes because the more hydrophilic TEOS layer was formed on the hydrophobic PE surface. The experiments for electrolyte uptake also indicated higher compatibility of the PE–SiO_2–TEOS separator: a 165.6% increase in weight was observed for the absorbed

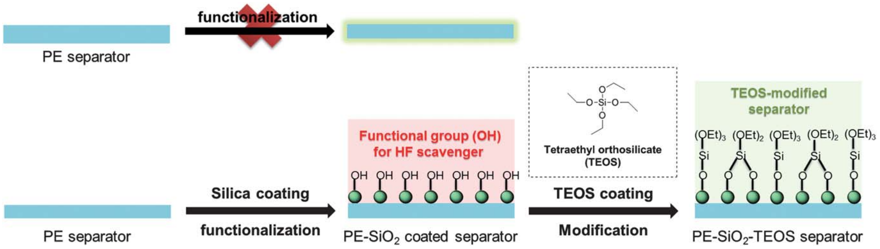
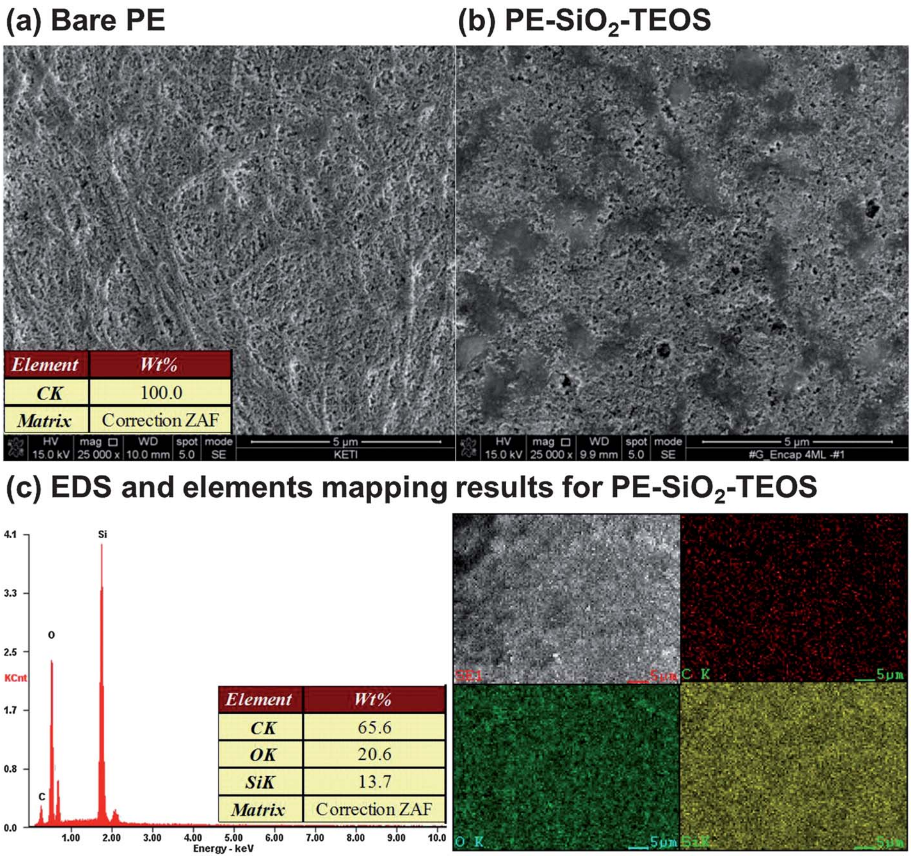


Fig. 1 Synthetic scheme for TEOS coated separator.



Element	*Wt%*
CK	100.0
Matrix	Correction ZAF

Element	*Wt%*
CK	65.6
OK	20.6
SiK	13.7
Matrix	Correction ZAF

Fig. 2 SEM images for (a) bare (b) PE–SiO_2–TEOS, (c) EDS and elements mapping results for PE–SiO_2–TEOS.

electrolyte in the separator, although the PE and PE–SiO_2 separators only exhibited 74.3% and 138.8% increase in weight, respectively. Because cycle performance of LIBs is considerably affected by their wettability with electrolyte, improved physical properties of the separator is expected to provide a positive influence on the LIB cycle performance.

Further FT-IR analysis provided informative spectroscopic evidences for the formation of a new layer, as shown in Fig. 3. The FT-IR spectrum of the PE–SiO_2–TEOS separator exhibits peaks corresponding to Si–O–CH_3 (880 cm^{-1}) and Si–O–Si (850–790 cm^{-1}, 478 cm^{-1}), which were formed as a result of free alcohol capping on the interlayer. These results confirm the formation of a HF scavenging multilayer with TEOS groups on the interlayer surface.

Prior to tests of the electrochemical performance of the modified separator, ionic conductivity and air permeability tests were performed to verify whether the TEOS layer formed on the surface had a significant effect on the resistance of the separator (Fig. S3 and S4†). Because an additional layer on the separator can act as an extra resistance factor as a result of disturbances in ion migration during the electrochemical process, an evaluation of these properties is necessary to estimate the electrochemical performance. According to the results, the ionic conductivity was slightly decreased in PE–SiO_2–TEOS (0.242 mS cm^{-1}) compared to PE (0.291 mS cm^{-1}) and PE–SiO_2 (0.269 mS cm^{-1}). These results agree well with the results for air permeability tests: PE–SiO_2–TEOS took longer for 100 cm^3 of air permeation (311.2 s) than PE (239.1 s) and PE–SiO_2 (285.6 s). These results indicate the resistance of PE–SiO_2–TEOS was slightly increased with formation of the TEOS layer, although it was confirmed that such increase would not lead to serious changes in utilization of LIBs.

To demonstrate the effect of the TEOS layer on the PE separator, electrochemical performance testing was conducted at an elevated temperature (60 °C), with $LiMn_2O_4$ as the cathode, graphite as the anode, and water-content-controlled electrolytes (1000 ppm) to accelerate HF generation in electrolytes (Fig. 4). The electrochemical cells were assembled with three kinds of separators, namely, bare PE separator (black), PE coated with SiO_2 (red), and PE coated with SiO_2-TEOS (blue). The cycle performance of the cell with bare PE showed drastic capacity fading, with only 45.8% retention after 50 cycles. On the other hand, the cell assembled with a SiO_2-coated PE separator showed improved cycle performance with higher retention (65.3%) after 50 cycles. More interestingly, the cell with a PE–SiO_2–TEOS separator showed much more improved cycle performance, exhibiting a high retention of 80.7% after 50 cycles. The observed outstanding electrochemical performance could be explained by considering the favorable interaction between HF and Si coated on the separator. The Si component effectively scavenges HF and increases the structural stability of the $LiMn_2O_4$ cathode, thereby resulting in enhanced cycle performance. The superior electrochemical performance of the PE–SiO_2–TEOS separator when compared to that of the PE–SiO_2 separator could have resulted from the difference in the chemical functionality developed on its surface. As shown in Fig. S5a in ESI,† the SiO_2 component in the interlayer could remove HF in the electrolyte as a result of the strong chemical bonds formed in Si–F by nucleophilic substitution reaction of F^-. However, the presence of an increased number of alcohol functional groups on PE–SiO_2 promoted the generation of HF by a nucleophilic substitution reaction with $LiPF_6$ (Fig. S5b†). This means that these two kinds of chemical reactions competed during the electrochemical process (HF scavenging reaction *vs.* HF generation reaction), leading to unremarkable cycle performance. On the contrary, the free alcohol groups of the interlayer on the PE–SiO_2–TEOS separator already participated in the formation of new local bonds (O–Si–C, outer layer). Therefore, there was less HF remaining in the electrolyte than in the case of the PE–SiO_2 separator owing to remarkable cycle performance.

These observations were further substantiated by ICP-MS analysis. The anode cycled with the PE–SiO_2–TEOS separator showed lesser Mn-ion dissolution (anode: 321.5 ppm, separator: 342.4 ppm) than with the bare PE separator (anode: 691.8 ppm,

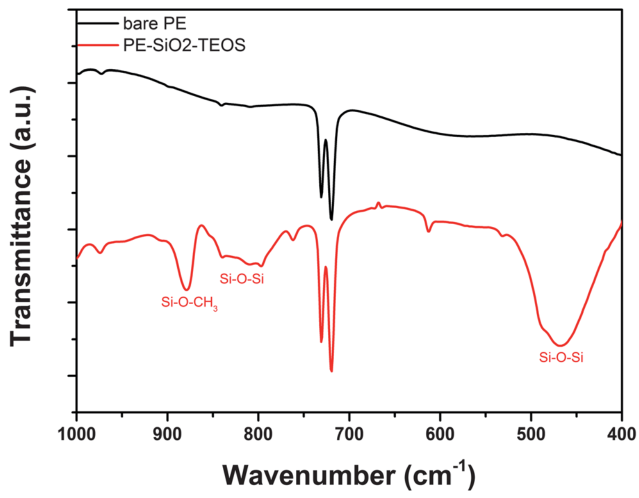


Fig. 3 Characterization of separator by FT-IR (black: bare PE, red: PE–SiO_2–TEOS).

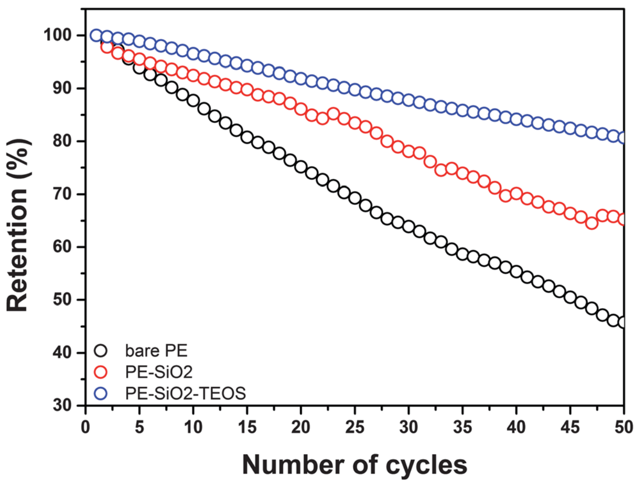


Fig. 4 Cycle performance results of graphite/$LiMn_2O_4$ full cell at 60 °C (a) bare PE (black) (b) PE–SiO_2 (red) (c) PE–SiO_2–TEOS (galvanostatically charged to 4.2 V and discharged to 3.0 V *vs.* Li/Li^+ with 0.5 C).

separator: 636.9 ppm) and the PE–SiO_2 separator (anode: 401.5 ppm, separator: 537.3 ppm). Mn-ion dissolution is mainly caused by cathode deterioration due to the reaction with HF in the electrolyte. Since the PE–SiO_2–TEOS separator is effective in scavenging the existing HF in the electrolyte, it leads to less dissolution of Mn ions from the cathode, thereby resulting in enhanced electrochemical performance of $LiMn_2O_4$ cathodes at higher temperatures.

The specific role of a functionalized separator was demonstrated by comparing the FT-IR spectra of the separator before and after cycling (Fig. 5). The main FT-IR peak corresponding to the existence of a TEOS layer (Si–O–C, 880 cm^{-1}, blue dot) almost disappeared after cycling. However, a new transmittance peak corresponding to Si–F bonding originated at 845 cm^{-1}.[26–28] This is an important spectroscopic evidence that explains the action of a TEOS layer on the separator, along with the disappearance of Si–O–C signals. According to the FT-IR results, the functionalized TEOS group is consumed by the chemical reaction with HF in the electrolyte, resulting in the formation of Si–F bonding. The relatively low intensity of signal corresponding to Si–F in the PE–SiO_2 separator indicates that the chemical reactivity of the TEOS group is more desirable for trapping HF than SiO_2 in the interlayer. Based on the spectroscopic evidence, a detailed illustration of the plausible reaction mechanism pertaining to the PE–SiO_2–TEOS separator is suggested in Fig. 6. Once the separator is exposed to the electrolyte consisting of HF, protonation of oxygen takes place spontaneously by a Bronsted acid–Lewis base reaction. Since the resulting oxonium intermediate is quite unstable, the remaining fluoride anions readily attack silicon to escape from the unstable oxonium state by recovering two electrons from silicon (bond breakage of Si–O). Repetition of this procedure effectively scavenges HF in the electrolyte, thereby preventing the deterioration of the $LiMn_2O_4$ cathode. Consequently, the cell with the TEOS-functionalized separator showed improved cycle performance. Further studies on this mechanism are underway.

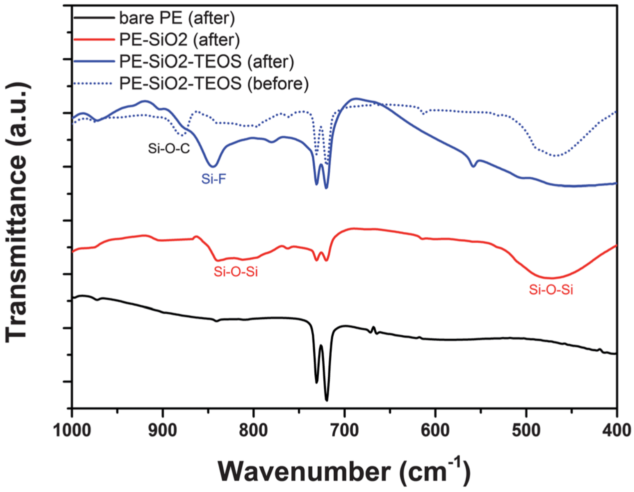


Fig. 5 FT-IR analysis of separator after cycling at 60 °C (black line: bare PE, red line: PE–SiO_2, blue line: PE–SiO_2–TEOS, blue dot: PE–SiO_2–TEOS (before cycling)).

In summary, we developed a novel synthetic methodology for the facile chemical modification of a PE separator and evaluated the cycle performance of $LiMn_2O_4$-cathode-based LIBs at high temperatures. For effective scavenging of HF in the electrolyte, the PE separator was modified by forming an interlayer consisting of OH groups that was subsequently converted to a siloxane chemical moiety (TEOS) *via* a simple alcohol–ester condensation reaction. The cell composed of the PE–TEOS separator showed excellent retention (80.7%) after 50 cycles. Systematic spectroscopic studies indicate favorable interaction between the scavenging layer and HF. ICP-MS results confirm lesser dissolution of Mn ions (anode and separator), and FT-IR analysis clearly indicates the formation of Si–F bonding as a result of a chemical reaction between the TEOS group and HF. Accordingly, we have also suggested a plausible mechanism underlying the chemical interaction between the PE–TEOS separator and HF. We believe that the novel approach proposed in this study will open up new opportunities to improve the electrochemical performance of Mn-based cathodes.

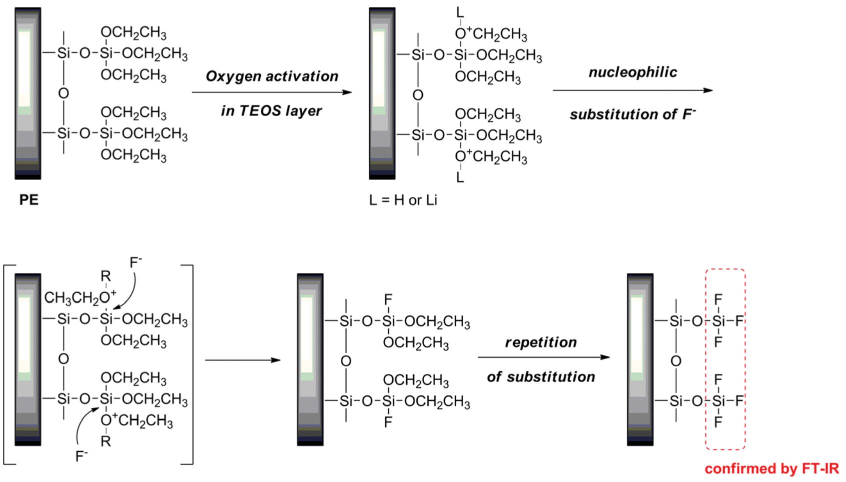


Fig. 6 Mechanistic consideration of HF scavenging by modified separator.

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