

Evaluate Sulfone-based Reduction Sensitive Electrolytes with Lithium $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ and Symmetric $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ Cells

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Energy is the essential resource for modern society, but recent growing concerns over limited fossil-fuel resources and pollution has introduced the need to use renewable energy at large scale. Lithium-ion batteries are seriously considered as a source of energy storage for future EVs, what means more security, more power and energy densities. One solution will be to associate a high voltage cathode like $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ or derivative with a low potential anode, which can incorporate both rapidly and easily lithium ions in its structure.¹ In standard batteries made from graphitic carbons, lithium plating and dendrite formation may occur at high power rate, leading to the risk of internal short circuits. Lithium titanate spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an alternative, which allows for reversible insertion of up to three lithium ions per formula unit at a potential of around 1.5 V vs. Li/Li^+ with a practical specific capacity around 160–175 mAh g⁻¹. Sulfones are known to be extraordinary anodic stable up to 5.5 V vs. Li/Li^+ .² These compounds are thus promising for high-potential applications but suffer from poor cathodic stability on carbonaceous anodes. To the best of our knowledge, sulfones such as TMS (Tetra Methyl Sulfone) and EMS (Ethyl Methyl Sulfone) have never been tested in $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ or $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells. To investigate on reduction stability of these compounds, it is necessary to remove metallic lithium for electrochemical tests. Consequently, $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ symmetric cells are introduced to evaluate sulfones during cycling, exclusively toward the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material.³

Alkylcarbonate- (EC/EMC 1M LiPF_6 , PC/EMC 1M LiPF_6) and sulfone-based (EMS/EMC 1M LiPF_6 , TMS/EMC 1M LiPF_6) electrolytes are here presented. In lithium and symmetric cells, low capacity losses are observed for the alkylcarbonate electrolytes due to high Li^+ conductivity and limited parasitic reactions at the electrode/electrolyte interfaces. Coulombic efficiencies are near to 1.00 upon 50 cycles for these two electrolytes in both $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ and $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ accumulators (Figs.1a and 1b). Sulfone-based electrolytes are oppositely unstable in half-cells, owing to EMS and TMS reaction on the lithium counter electrode (Fig.1c and 1d). This results in a polarization increase caused by the formation of resistive electrode/electrolyte interfaces. In the case of symmetric cells, perfect flat plateaus corresponding to the $\text{Ti}^{+III} \leftrightarrow \text{Ti}^{+IV}$ redox couple and low polarization ($\Delta E=i.R$) are observed. This means that the two $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /electrolyte interfaces bring low reactivity even if sulfones are used. However, the measured coulombic efficiencies are 0.05% lower compared to alkylcarbonates and undesirable reactions are still present. Lifetime of batteries with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode material can be handicapped by EMS and TMS use in electrolytes, and alkylcarbonates are the best compositions up to now.

The presented study will be a comparison between alkylcarbonate- and sulfone-based electrolytes (1M LiPF_6) in half- and symmetric cells using potentiostatic/galvanostatic experiments and ex-situ electrode surface characterizations (SEM, FT-IR/ATR and XPS).

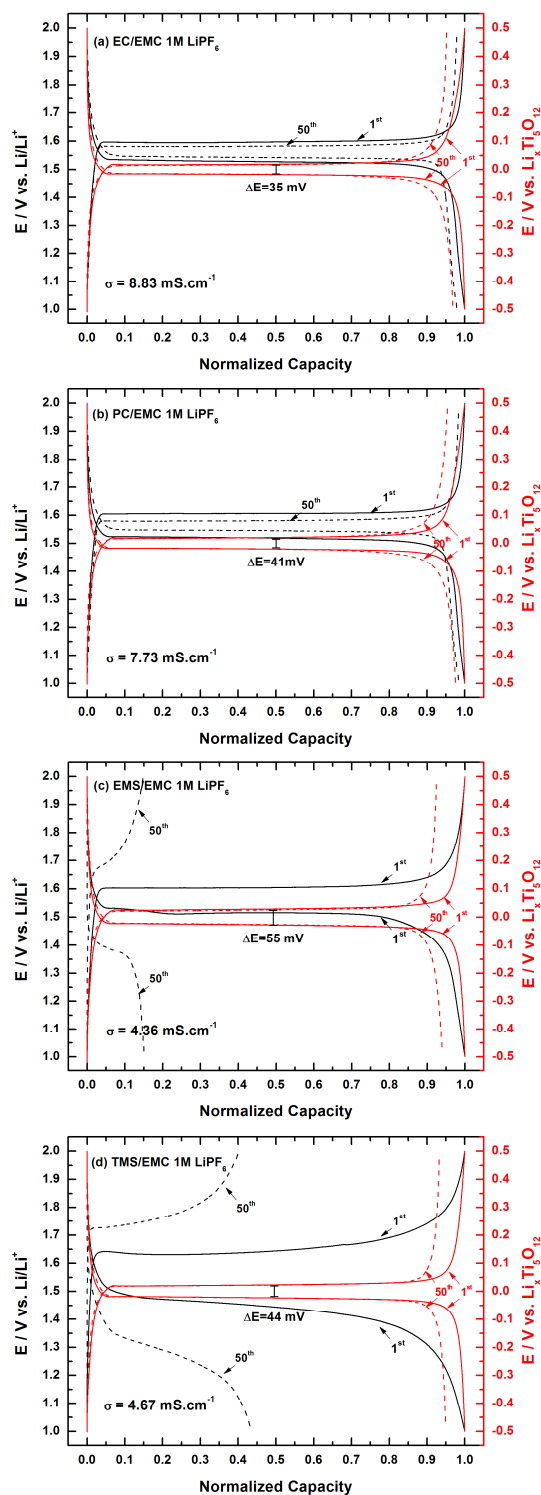


Figure 1. Normalized delithiation and lithiation capacities for $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ (in black) and $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells (in red) using (a) EC/EMC 1M LiPF_6 , (b) PC/EMC 1M LiPF_6 , (c) EMS/EMC 1M LiPF_6 and (d) TMS/EMC 1M LiPF_6 as electrolytes.

References

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