Mitigating HF in Quasi-solid State Electrolytes via Cerium Oxide Functionalized Nanoparticles

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Introduction

The increasing reliance on renewable energy sources has amplified the demand for more efficient energy storage systems. Quasi-solid state electrolytes (QSSE) enable the replacement of graphite anodes with metallic lithium anodes, offering significant improvements in both performance and capacity. A QSSE can be prepared by incorporating a lithium salt into a polymer that retains a minimal amount of solvent, which promotes Li-ion conduction. Typically, salts containing fluorine-based anions are employed, but these anions undergo hydrolysis in the presence of water, producing HF that subsequently degrades the cathode. This study aimed to explore the use of functionalized cerium oxide nanoparticles as HF scavengers in Polyvinylidene fluoride–Hexafluoropropylene based QSSE[1], with the goal of preventing cathode damage and improving battery stability.

HF Formation Reactions

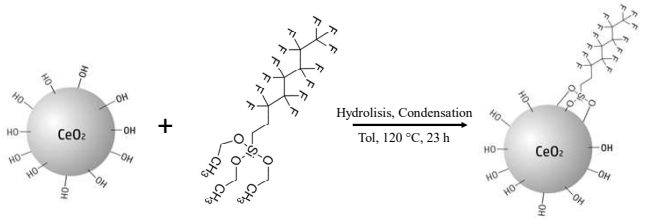
$$LiPF_6 + H_2O \Rightarrow LiF + POF_3 + 2HF$$

$$POF_3 + H_2O \Rightarrow HPO_2F_2 + HF$$

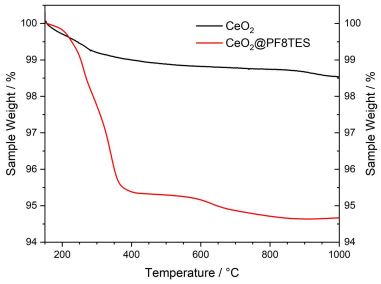
$$HPO_2F_2 + H_2O \Rightarrow H_2PO_3F + HF$$

$$H_2PO_3F + H_2O \Rightarrow H_3PO_4 + HF \quad [2]$$

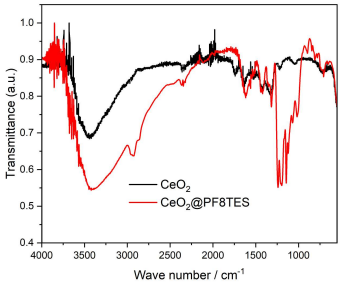
Functionalization reaction



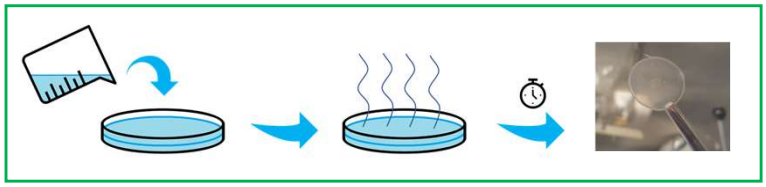
Thermogravimetry



IR Spectroscopy

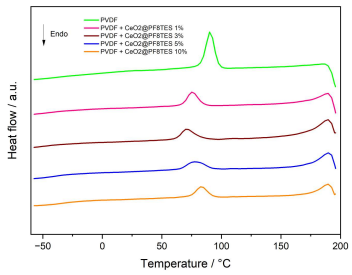


Membrane Preparation

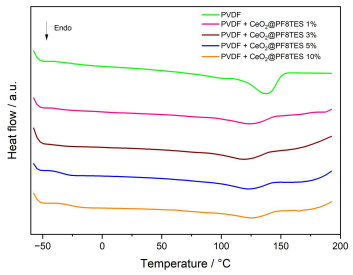


The PVdF-HFP membranes were fabricated using the solvent casting technique, employing THF and DMF as solvents, Lithium bis(fluorosulfonyl)imide, and functionalized Cerium Oxide nanoparticles. All steps were carried out in an argon-filled glove box, and the drying process was maintained for 72 hours.

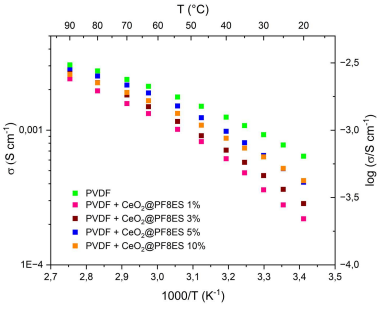
DSC (Cooling)



DSC (Heating)

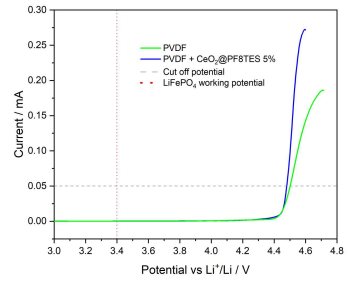


Arrhenius Plot



(SS | PVdF-HFP + LiFSI + CeO_2@PF8TES | SS)

Linear Sweep Voltammetry

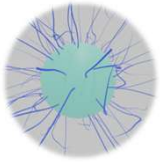


(SS | Li | PVdF-HFP + LiFSI + CeO_2@PF8TES | SS)

Conclusions and Perspectives

- ✓ The surface of commercial cerium oxide nanoparticles successfully functionalized with Perfluorooctyl triethoxysilane, as confirmed by TGA analysis.
- ✓ The combination of functionalized nanoparticles and PVdF-HFP allowed to obtain a membrane that could act as quasi-solid-state electrolyte, with a filler content varying between 0% (only PVdF-HFP) and 10%. Showing a good ionic conductivity with a filler content around **5%**.
- ✓ As shown in Linear Sweep Voltammetry, the stability window of the membrane with and without filler is very similar.

Future experiments will be carried out on a full cell, including controlled exposure to moisture, in order to better assess the scavenging effect of the Cerium Oxide.



References

[1] Rui, Z. & Liu, J. Understanding of free radical scavengers used in highly durable proton exchange membranes, *Progress in Natural Science: Materials International*, 30 (2020), 732
[2] Magistris, Aldo, et al. "Transport and thermal properties of (PEO) n–LiPF6 electrolytes for super-ambient applications." *Solid state ionics* 136 (2000): 1241-1247.