Organic-Inorganic Hybrid Solid Composite Electrolytes Combine Functionality, Manufacturability, and Electrode Compatibility

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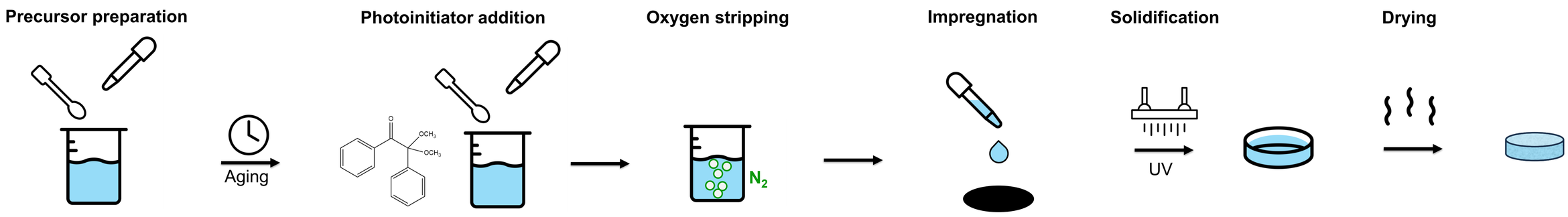
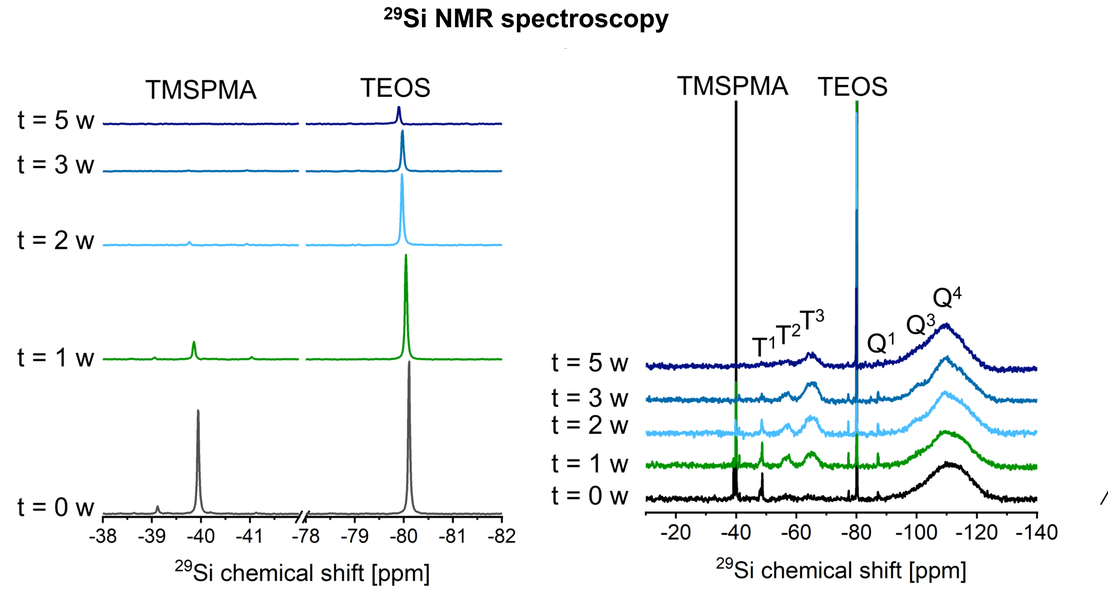
Introduction

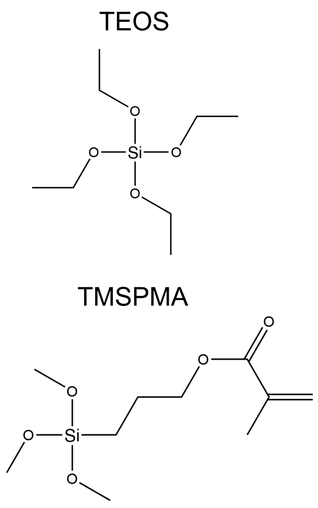
- Ionic liquid electrolytes can be incorporated into a solid matrix to form solid composite electrolytes (SCEs) or ionogels.
- For commercial viability, SCEs must be manufacturable, which can be achieved through liquid processing. Here, a precursor solution is impregnated into a porous electrode and rapidly solidified, ensuring intimate electrode/electrolyte contact.
- Polymer-based SCEs offer good manufacturability but suffer from low ionic conductivity, whereas silica-based SCEs can achieve higher conductivity. Traditional non-hydrolytic silica synthesis requires acids that damage electrodes, while hydrolytic synthesis avoids acids but suffers from spontaneous and slow solidification, limiting manufacturability.
- This work presents a hybrid SCE that combines functionality, electrode compatibility, and manufacturability.

Electrolyte Synthesis



Aging

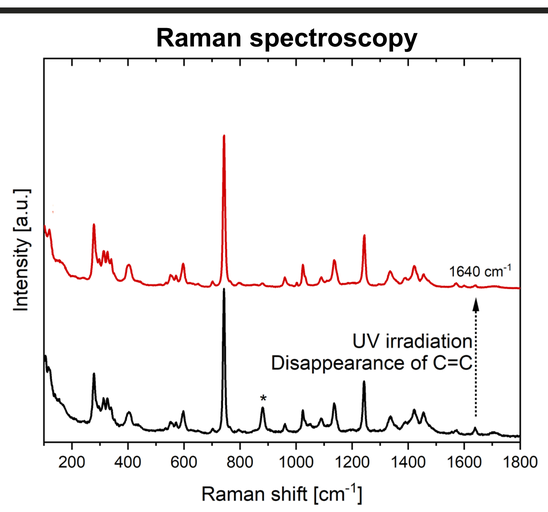


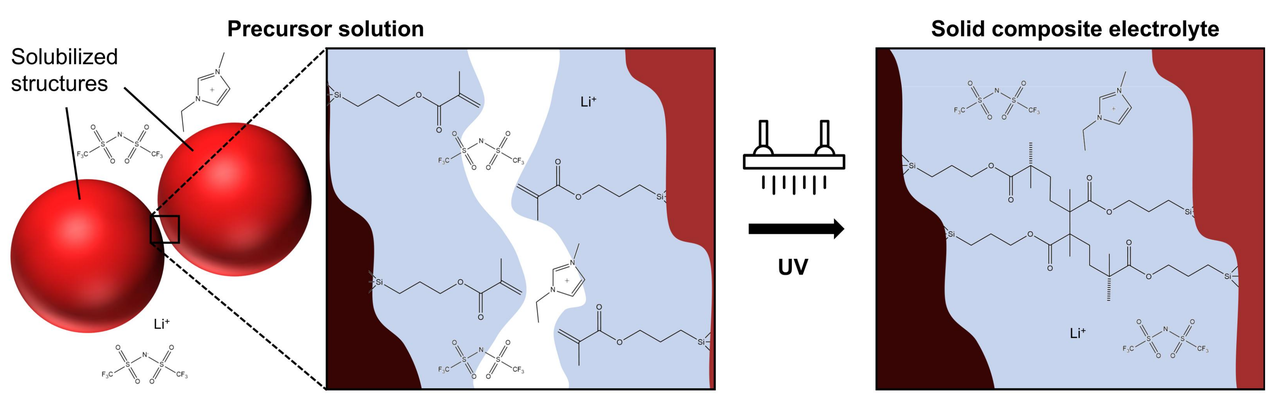


- The hydrolysis and condensation of TMSPMA is significantly faster than that of TEOS.
- "T" designates trifunctional units (i.e. TMSPMA). The codes T^1, T^2, and T^3 signify that these units are condensed with one, two, and three other alkoxysilanes, respectively. Similarly, the codes Q^1, Q^2, Q^3, and Q^4 are used for TEOS units that are condensed with one, two, three and four other alkoxysilanes, respectively.
- Already immediately after mixing, there is a significant T^1 signal, indicating that TMSPMA rapidly undergoes hydrolysis and condensation. This indicates that the beginning of the aging reaction mainly involves the self-condensation of TMSPMA molecules, with only a small amount of TEOS being incorporated. After one week of aging, a significant amount of T^3 structures (i.e., fully condensed TMSPMA) has been formed. After five weeks, the TMSPMA and TEOS molecules have mostly been converted into T^3 and Q^4 structures.

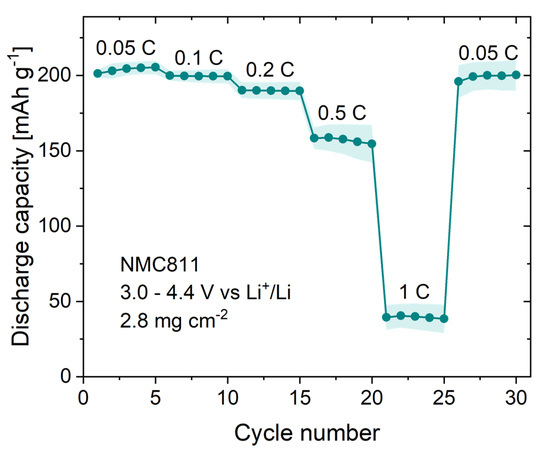
Solidification

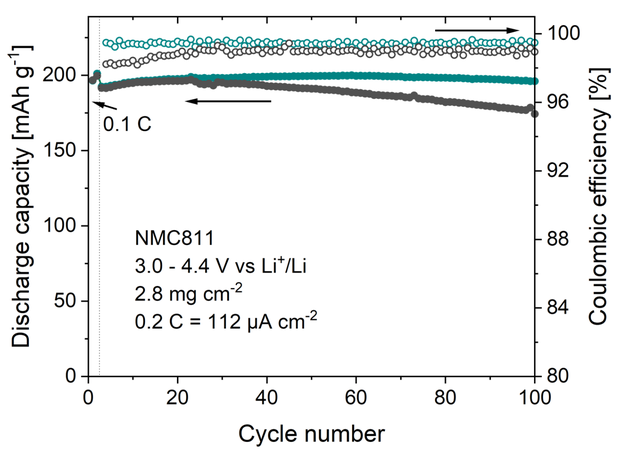
- The solidification process is induced by the crosslinking of separate silica structures through the polymerizable moieties present on the organosilane chains.





Electrochemistry





- The solid electrolytes were incorporated into NMC811/Li half-cell coin cells by impregnating the precursor solution into a stack of an electrode punch and a glass fiber separator, followed by UV irradiation and drying in a dry room (until no more mass loss could be observed).
- These cells reach 209, 199, and 190 mAh g^{-1} at 0.05 C, 0.1 C, and 0.2 C respectively. The capacity at higher currents is limited by the lithium negative electrode, reaching 158 mAh g^{-1} at 0.5 C and 40 mAh g^{-1} at 1 C.
- The reproducibility was assessed in cycle stability tests, where two cells had an initial discharge capacity of 192 mAh g^{-1} (third cycle, 0.2 C), and retain 100% and 91.1% of this capacity in the 100th cycle.

Conclusions

- We describe a novel type of hybrid SCE as solid electrolyte in lithium batteries, which combines functional properties with electrode compatibility and good manufacturability. The acid-free precursor solution can be readily impregnated into porous electrodes without damaging them and can then be instantaneously solidified by irradiation with UV light.
- NMC811/Li cells have a high electrochemical stability, retaining 91-100% of their initial capacity after 100 cycles (0.2 C).
- The combination of functional properties, electrode compatibility, and manufacturability shows that this type of SCE is a potential candidate for the further development of solid-state lithium metal battery technology, provided that its compatibility with lithium metal can be further improved.

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