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## ARTICLE

## Pyrrrolidinium-based Gel Composites for Reprocessable, Flame-Retardant Electrolytes

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Flame retardant and reprocessable gel composites composed of a pyrrolidinium-based poly(ionic liquid) were successfully prepared by incorporating surface-modified nanoparticles functionalized with ionic liquids or ureidopyrimidinone groups. Covalent functionalization was verified through CP-MAS <sup>29</sup>Si NMR, FT-IR, and thermogravimetric analysis. Surface modified NPs significantly improved the dynamic characteristics of synthesized gel composites, yielding composites with enhanced reprocessability and remarkable mechanical flexibility, reaching elongation at break up to 460%, solely through reversible dynamic interactions without the need for permanent covalent crosslinking. Upon reprocessing the ionic conductivity of gels was efficiently restored, reaching values of  $2.2 \times 10^{-4} \text{ S-cm}^{-1}$  at room temperature. The composites further exhibited excellent thermal stability up to 330 °C, and an inherently flame-retardant nature classified as UL 94 V-0 grade. These combined features underscore the potential of the developed PIL-based gel composites for safe, durable, and high-performance applications in electrochemical and flexible devices.

### Introduction

Lithium-ion batteries (LIBs) have become an indispensable part of modern life. Major progress has been made in improving their performance, durability, and efficiency over the past few decades.<sup>1,2</sup> However, safety remains a persistent concern linked to the organic solvent-based electrolytes used in most commercial batteries. Flammability of these electrolytes can pose serious fire hazards, especially when exposed to mechanical/thermal/electrical misuse or when lithium dendrites form during cycling, which can trigger thermal runaway.<sup>3</sup> Material recyclability/reprocessability is another critical factor, particularly as global reliance on energy storage devices is rapidly increasing.<sup>4, 5</sup> Researchers have been developing alternative electrolyte materials that can resolve reprocessability/recyclability concerns and safety aspects while maintaining or even enhancing performance.<sup>6, 7</sup> Ionic liquids (ILs) and poly(ionic liquid)s (PILs) in particular have emerged as promising candidates.<sup>8, 9</sup> They offer wide electrochemical stability windows, good ionic conductivity, and inherent non-

flammability. Converting these liquid electrolytes into solid or gel-like materials opens new opportunities for advanced energy-storage systems, including flexible and reprocessable energy storage designs.<sup>10-12</sup> PILs combine the structural advantages of polymers with the ionic conductivity of ILs. They are particularly appealing because they can form stable, solvent-free electrolytes with excellent thermal and electrochemical properties.<sup>13, 14</sup> In addition, their tunable chemical structure allows for fine adjustment of mechanical strength, ion transport pathways, and interfacial compatibility with electrodes. However, PILs are still limited in practical use due to lower conductivity than that of liquid electrolytes. Embedding dynamic bonds in these systems can be a possible strategy to significantly enhance performance and material properties. These reversible covalent or non-covalent interactions can break and reform under external stimuli, enabling self-healing, recycling, and reprocessing. Dynamic covalent chemistries such as boronic ester, imine, and disulfide exchange are commonly used for generating vitrimeric electrolytes, where bond selection controls dynamic properties, activation energy, reprocessing conditions, and self-healing efficiency.<sup>15, 16, 17</sup> Supramolecular interactions in polymer networks promote self-healing and reprocessability, with hydrogen bonds being the one of the most studied.<sup>18, 6</sup> In parallel, nanofillers represent another effective way to boost electrolytes properties, especially in terms of conductivity and mechanical strength. Inorganic fillers such as aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), and titanium oxide (TiO<sub>2</sub>) have been widely incorporated into polymer matrices like polyethylene oxide (PEO) to form polymer composite electrolytes.<sup>19-21</sup> Surface modification of these nanoparticles can further improve their dispersivity and strengthen their interactions within the

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polymer network, leading to better overall material properties.<sup>22-24</sup>

In this study, we report the development of flame-retardant, stretchable, reprocessable, and conductive materials based on dynamic poly(ionic liquid) network composites. Gel polymer electrolytes require reprocessing not only from a sustainability perspective but also to enhance the practical lifetime and economic viability of advanced battery systems. In addition, during battery manufacturing, processing defects such as incomplete wetting, film imperfections, or inhomogeneous thickness may occur. Reprocessable gel electrolytes therefore allow correction of defects without complete disposal of the material, so significantly improving manufacturing efficiency. The design strategy is centered around silica nanoparticles whose surfaces were modified with two different functional groups to impart compatibility with the surrounding matrix. Firstly, ureidopyrimidinone (UPy), forming strong and reversible quadruple hydrogen bonds were embedded, that create dynamic crosslinks and enhance mechanical properties.<sup>25-27</sup> The second type of modification introduces ionic liquid moieties, which improve nanoparticle dispersibility and promote ionic interactions throughout the polymer network.<sup>24, 28-30</sup>

Our approach focuses on formulating PIL gels and composites that combine safety, flexibility, and high ionic conductivity. Pyrrolidinium-based ionic liquids and corresponding monomers were chosen due to their outstanding electrochemical and thermal stability.<sup>31</sup> The influence of silica nanofillers with different surface chemistries on the structural and electrochemical behavior of the gels was systematically explored. A schematic overview of the designed gel structure is shown in Figure 1, illustrating the main components: a pyrrolidinium-based acrylate monomer that polymerizes to form the PIL backbone. A UPy monomer, integrated into the polymer network to introduce reversible supramolecular interactions that enhance reprocessability and mechanical resilience. The mobile ionic phase, consisting of a pyrrolidinium-based ionic liquid (PMPyrr TFSI) and lithium salt (LiTFSI), providing the primary ionic conduction pathway. The surface-modified silica nanofillers, acting as a reinforcing agent promoting dynamic crosslinking and high stretchability. A photoinitiator to enable UV-curing during material fabrication. This work aims at a versatile design concept for multicomponent PIL-based composite gels that unite safety, flexibility, and high ionic mobility.



Fig. 1. Gel components and schematic representation of gel composite.

## Experimental

### Materials and instrumentation

All chemicals were used as received from Sigma Aldrich, TCI, Alfa Aesar, abcr and Io-li-tec unless otherwise stated. DCM and chloroform were dried by refluxing over calcium hydride prior to use. Dry DMF and ACN were collected from solvent purification system (mBraun SPS5).

Cross-polarization (CP) magic-angle spinning (MAS) solid state NMR of <sup>29</sup>Si were recorded at ambient temperature on a Bruker Avance II 400 spectrometer, 4 mm MAS probe, MAS 5 kHz, CP time of 10 ms and repetition delay of 5s.

Thermogravimetric analysis (TGA) was conducted on Netzsch TG 209 F3. Samples (5-15 mg) were placed in alumina crucibles and heated from 35 °C to 800 °C with the heating rate of 10 K min<sup>-1</sup> under nitrogen atmosphere (flow rate 20 mL min<sup>-1</sup>). The NETZSCH Proteus was used for analyzing the recorded data.

Fourier-transform infrared spectroscopy (FT-IR) analysis was conducted using attenuated total reflection technique on VERTEX 70 v FT-IR Spectrometer (Bruker) equipped with the golden gate diamond ATR unit. Measurements were conducted

at room temperature, and covered spectral range from 550 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

Dynamic Light Scattering (DLS) was measured using a Litesizer 500 (Anton Paar) equipped with a wavelength 658 nm, 40 mW single-frequency laser diode. All data were processed using Kalliope software.

Negative-stain TEM grid preparation and imaging: Continuous carbon copper grids (200 mesh; Formvar-supported) were glow-discharged (Pelco easyGlow; 30 s; air; standard settings). Subsequently, 3 μL of sample was applied to each grid and incubated for 1 min. Excess liquid was removed by side blotting with filter paper. Then, grids were washed by floating them on drops of distilled water three times for 1 min each. For negative staining, grids were floated on a drop of 2% (w/v) aqueous uranyl acetate for 1 min and side blotted. For each sample, grids were prepared with uranyl acetate staining and without stain (omitting the uranyl acetate step after the water washes) to control for staining artefacts. Prepared grids were stored in grid boxes until imaging. Images were acquired on a Zeiss EM900 transmission electron microscope operated at 80 kV using a 1k slow scan CCD camera (TRS Restlichverstärkersysteme).



Tensile test was conducted with INSTRON 5900 Series universal testing system machine. Dumbbell samples (ISO 37 Type 2) were produced by a pneumatic cutter (P-VS 3000, MonTech Rubber Testing Solutions). Measurements were performed at room temperature at a strain rate of 20 mm·min<sup>-1</sup>. Data analysis was performed *via* Bluehill Universal (version 4.08).

Broadband Dielectric Spectroscopy (BDS) was used for investigating ionic conductivities on Novocontrol "Alpha analyzer". PIL gels were placed between two brass electrodes ( $d = 20$  mm), and the thickness of each sample gel was measured individually (sample thickness ranged from 0.20 mm to 0.50 mm). Measuring cell was placed in a cryostat with a constant flow of dry nitrogen. Ionic conductivity was recorded in the frequency range 1 – 10<sup>6</sup> Hz and different temperatures. Ion conductivity values were extracted from the plateau of  $\sigma$  vs.  $T$ .

Reprocessing of gel composites were done using vacuum compression molding (VCM) from MeltPrep. Sample was placed in the VCM disc tool with the diameter of 20 mm and heated at 120 °C for 3 hours. Subsequently tool was placed of the cooling unit and restored sample was removed.

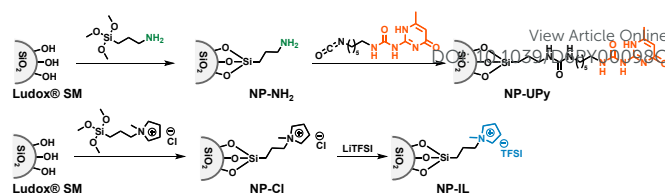
## Synthesis

1-(3-(acryloyloxy)propyl)-1-methylpyrrolidin-1-ium bis(trifluoromethylsulfonyl)amide (**M-IL**) and 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl acrylate (**M-UPy**) was synthesized in three step reaction reported previously.<sup>32,33</sup> The corresponding procedures are described in detail in the Supplementary Information, together with the full characterization data (for NMR spectra, see Figures S1–S7).

## Surface modification of nanoparticles

Surface modification of NPs was done according to **Scheme 1**. **NP-UPy** was prepared in a two-step reaction: In the first step 3 g of Ludox® SM solution was diluted with deionized water to 100 mL. The mixture was kept for stirring and heated to 80 °C, followed by the gradual addition of 0.9 g (5 mmol) of 3-(trimethoxysilyl)propan-1-amine *via* syringe. The reaction was maintained under continuous stirring at 80°C for 48 h. Upon completion, the resulting dispersion was concentrated with rotavapor. The concentrated colloid was then precipitated in acetone. Obtained **NP-NH<sub>2</sub>** were separated from the solvent with centrifuge, washed 3 times using acetone and subsequently dried in oven at 60 °C under vacuum.

In the second step 1 g of **NP-NH<sub>2</sub>** (1 g) was dispersed in dry CHCl<sub>3</sub> (100 mL) and subsequently 1-(6-isocyanatoethyl)-3-(4-methyl-6-oxo-1,6-dihydropyrimidin-2-yl)urea (**UPy-NCO**) (0.62 g, 2.1 mmol, previously synthesized according to the literature<sup>34</sup>) was added. The reaction was refluxed under inert atmosphere for 24 h. The modified particles were washed with CHCl<sub>3</sub> for removing unreacted (6-isocyanatoethyl)-3-(4-methyl-6-oxo-1,6-dihydropyrimidin-2-yl)urea. **NP-UPy** was collected by centrifuge and dried in oven in 60 °C under vacuum. (1.2 g of product obtained)



**Scheme 1.** Surface modification of Ludox® SM with IL and UPy groups.

**NP-IL** was prepared by previously described procedure.<sup>29</sup> Initially N-[3-(trimethoxy silyl)propyl]-N-methylpyrrolidinium chloride was prepared with the following procedure: N-methylpyrrolidinium (5 mL, 47 mmol) and (3-chloropropyl)trimethoxysilane (8.57 mL, 47 mmol) mixture was kept at 80 °C while stirring for 48 hours under inert atmosphere. Red/orangish mixture was washed using diethyl ether (4 times) and obtained product was dried in vacuum. Yield 45%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$  in ppm): 3.78 – 3.61 (m, 4H), 3.54 – 3.47 (m, 2H), 3.45 (s, 9H), 3.19 (s, 3H), 2.27 – 2.08 (m, 4H), 1.80 – 1.68 (m, 2H), 0.61 – 0.53 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz,  $\delta$  in ppm): 65.36, 64.15, 50.62, 48.40, 21.5, 17.59, 5.77.

Silica nanoparticles Ludox-sm® solution (3 g) was diluted in deionized water (100 g) and 0.7 g (2.5 mmol) of N-[3-(trimethoxysilyl)propyl]-N-methylpyrrolidinium chloride was added to the solution. The mixture was kept stirring at 80°C for 24 hours. Modified nanoparticles were concentrated using a rotary evaporator and precipitated into acetone. **NP-Cl** were collected using centrifugation and washed with acetone three more times. Subsequently **NP-Cl** (4.5 g) were dissolved in 120 mL deionized water and mixed with 20 mL of solution containing 4 g (14 mmol) LiTFSI. The mixture was kept for stirring for 8 hours at room temperature, after which the final product was collected *via* centrifugation and washed with deionized water (4 times). **NP-IL** was dried under vacuum at 70 °C for 24 hours.

PIL gel composite preparation:<sup>32</sup> In a typical gel preparation procedure initiator (DMPA), **M-IL**, **M-UPy** and modified nanofillers (**NP-IL** or **NP-UPy**) were weighed in a dried vial equipped with a magnetic stirring bar. Ionic liquid (PMPyrr TFSI) and lithium salts (LiTFSI) were added into the vial in the glovebox. The vial was taken out of glove box and dry DCM was rapidly added as solvent and the vial was sealed with the screw cap. The mixture was stirred till the solid part was totally dissolved. The mixture was then transferred to a one-neck flask rapidly, the DCM was removed by rotavapor at RT under vacuum. The gel precursor was transferred into a glove box, spread evenly on a petri dish and polymerized under UV light ( $\lambda=365$  nm) for 1h. The final polymerized film was removed from the petri dish carefully and cut into different specimens in glovebox for the subsequent characterizations.

## Results and discussion

### Surface modification of nanoparticles

To prepare the gel composites, the initial step involved modification of commercially available silica nanoparticles (Ludox® SM) for introducing ionic liquids groups or supramolecular moieties (UPy) on the surface. Following the



modification and purification procedures described in the Experimental Section, the obtained NPs (Fig. 2A) were thoroughly characterized by  $^{29}\text{Si}$  CP-MAS NMR, TGA, and FT-IR spectroscopy. Fig. 2B shows the  $^{29}\text{Si}$  CP-MAS spectra before and after surface modification. The appearance of new peaks at  $-68$  and  $-58$  ppm indicates the covalent attachment of organic moieties to the silica surface. According to conventional

nomenclature, these peaks correspond to  $\text{T}_3$  ( $\text{RSi}(\text{O}_{0.5})_3$ ) and  $\text{T}_2$  ( $\text{RSi}(\text{O}_{0.5})_2$ ), where R represents the covalently attached organic group.<sup>35–37</sup> The higher intensity of the  $\text{T}_3$  signal suggests that most surface species are bound through three siloxane linkages to the nanoparticle surface.

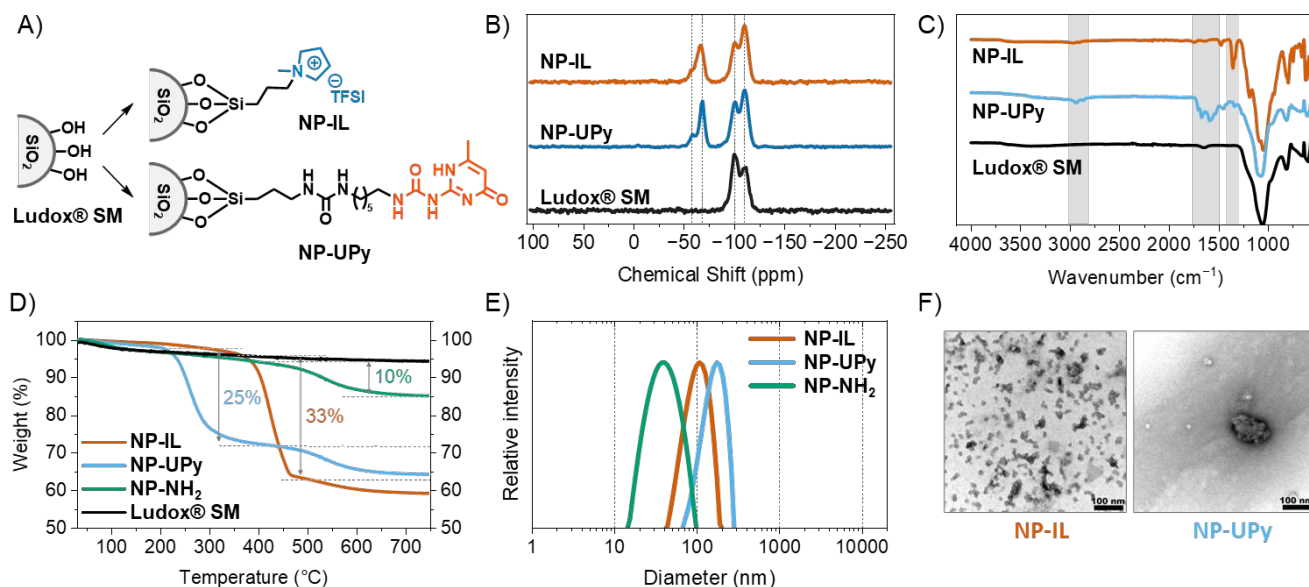


Fig. 2 A) Chemical structure of surface modified NPs B)  $^{29}\text{Si}$  CP MAS solid state NMR, C) thermogravimetric analysis, D) FT-IR spectra of surface modified nanoparticles, E) size distribution of surface modified NPs and F) corresponding TEM images.

Additionally, the decrease in the  $\text{Q}_3$  peak intensity (around  $-100$  ppm) after modification indicates a reduction in the number of silanol groups, which is consistent with successful covalent functionalization of the silica nanoparticles. Fig. 2C shows the IR spectra of the nanoparticles, highlighting the appearance of alky C–H stretching vibrations ( $2800\text{--}3000\text{ cm}^{-1}$ ) after surface modification. **NP-IL** exhibits characteristic bands of the TFSI<sup>−</sup> counterion at  $1349\text{ cm}^{-1}$  ( $\text{SO}_2$  stretching) and  $1179\text{ cm}^{-1}$  ( $\text{CF}_3$  stretching).<sup>38, 39</sup> On the other hand, **NP-UPy** shows the new bands in the  $1400\text{--}1700\text{ cm}^{-1}$  region, corresponding to C=O, C–N, and N–H bond vibrations, confirming successful functionalization.<sup>40–42</sup> Thermogravimetric analysis was employed to quantify the degree of surface modification (Fig. 2D), assuming that the observed weight loss primarily arises from the degradation of the organic surface layer, while contributions from moisture evaporation and dihydroxylation are neglectable. The TGA thermograms (Fig. 2D) display the mass loss of Ludox-sm<sup>®</sup>, **NP-NH<sub>2</sub>**, **NP-UPy**, and **NP-IL**. Based on these values the concentration of ionic liquid functional groups in **NP-IL** was calculated to be  $0.81\text{ mmol/g}$ , while **NP-UPy** exhibited functional group concentrations of  $0.68\text{ mmol/g}$ . Ludox SM is reported to have a specific surface area of  $320\text{--}400\text{ m}^2/\text{g}$ . According to literature, the surface silanol density can be approximated as 5 OH per  $\text{nm}^2$ ,<sup>43</sup> so estimating the total number of hydroxyl groups of Ludox SM to be  $(1.6\text{--}2.0)\times 10^{21}$  OH per gram, corresponding to  $2.66\text{--}3.32\text{ mmol/g}$ . Since we cannot exactly assess the fractions of the bi- ( $\text{T}_2$ ) or tri- ( $\text{T}_3$ ) siloxane linkages, the precise extent of the surface modification is difficult to determine. Assuming that attachment sites with  $\text{T}_3$

predominate, the estimated extent of surface modification is  $85\text{--}91\%$  for **NP-IL** and  $61\text{--}77\%$  for **NP-UPy**.

Nanoparticle size was monitored throughout the modification process to ensure that the particles remained within the expected range. The starting material (Ludox<sup>®</sup> SM) with an average particle diameter of  $7\text{ nm}$ , exhibited a gradual increase in size after each functionalization step. **NP-NH<sub>2</sub>** showed the smallest average diameter, followed by **NP-IL** and **NP-UPy**. Dynamic light scattering (Fig. 2E) analysis indicated that **NP-UPy** exhibited hydrodynamic diameter exceeding  $100\text{ nm}$ , which is attributed to supramolecular aggregation driven by the strong UPy-UPy interactions. This clustering behavior was further verified by transmission electron microscopy (Fig. 2F) which showed the presence of aggregated domains. In contrast, **NP-IL** exhibited a smaller hydrodynamic radius, consistent with the TEM observations of well-dispersed particles and reduced aggregation (for comparison see also ESI, Figures S9 and S10).

#### Gel composite preparation

Compositional optimization and dynamic crosslinking are critical to PIL-based gel performance for achieving high ionic conductivity and enabling simultaneous self-healing by reversible noncovalent interactions. In a typical synthesis, the multicomponent gel is prepared by first formulating a precursor mixture containing the IL-functionalized monomer (**M-IL**), the UPy-based monomer (**M-UPy**), ionic liquid (IL), lithium salt, and nanoparticles (for generating gel composites). The homogenous



mixture is subsequently polymerized *via* photopolymerization to yield a self-standing, transparent gel film (Fig. 3).<sup>32</sup>

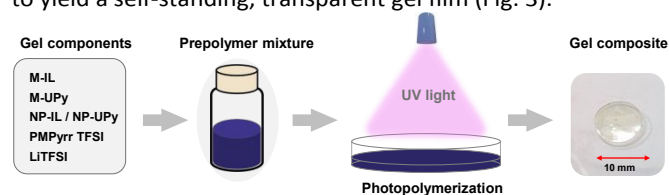


Fig. 3. Schematic representation of gel electrolyte preparation.

In our previous investigation, devoid of NPs the formulations included 1,6-hexanediol dimethacrylate as a covalent crosslinker. Covalent crosslinker effectively enhanced the gel's stretchability, but it simultaneously reduced its ability to self-heal or be reprocessed due to the formation of permanent networks. In the present work, we eliminated 1,6-hexanediol dimethacrylate crosslinker to promote dynamic and reversible interactions, compensating for the potential loss in mechanical strength by incorporating surface-modified nanofillers.

Table 1. Gel composite compositions with varying content of NP-IL and NP-UPy and their corresponding properties.

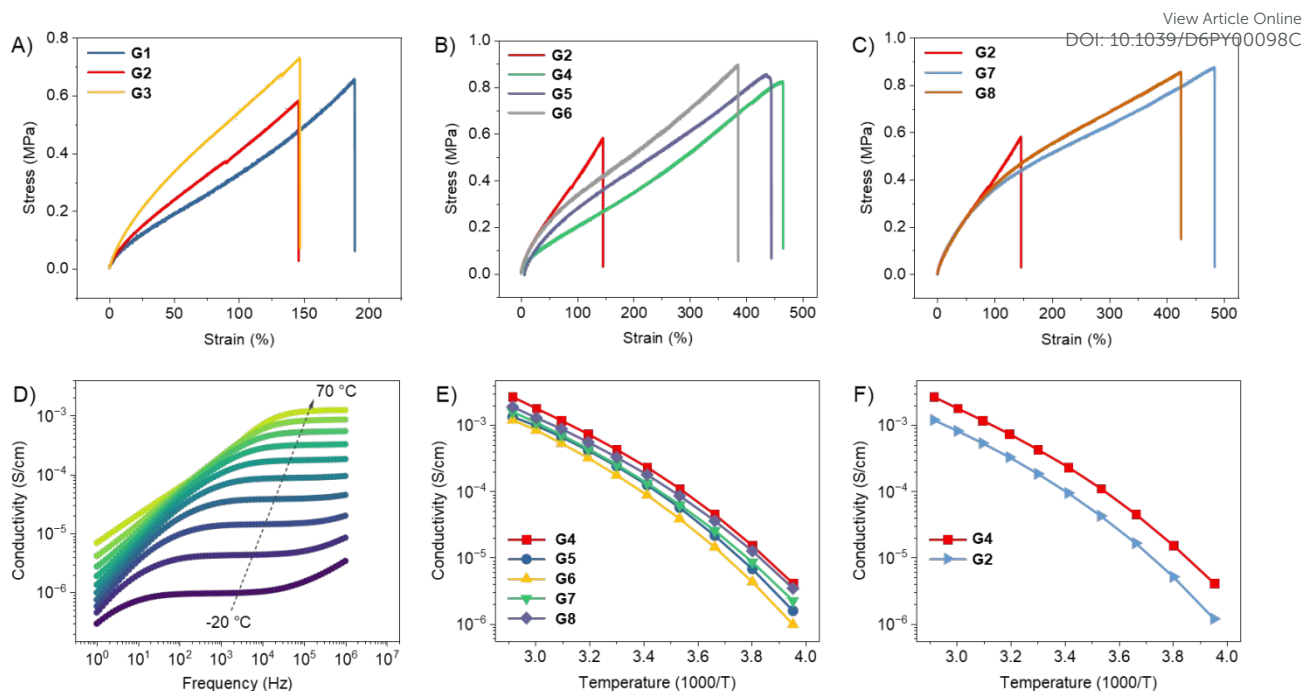
| Sample | Covalent Crosslinker | Molar Ratios |       |   | IL (wt%) | Li salt (wt%) | Nanofiller | Nanofiller Amount (wt%) | Conductivity at RT ( $S\text{ cm}^{-1}$ ) | Tensile Strength (MPa) | Elongation at Break (%) |
|--------|----------------------|--------------|-------|---|----------|---------------|------------|-------------------------|---|------------------------|-------------------------|
|        |                      | M-IL         | M-UPy | C |          |               |            |                         |   |                        |                         |
| G1     | +                    | 10.4         | 8     | 1 | 48.7     | 16.3          | –          | –                       | $1.1 \times 10^{-4}$                      | 0,66                   | 189                     |
| G2     | +                    | 10.4         | 8     | 1 | 46.3     | 15.4          | NP-IL      | 5                       | $9.5 \times 10^{-5}$                      | 0,58                   | 145                     |
| G3     | +                    | 10.4         | 8     | 1 | 43.5     | 14.6          | NP-IL      | 10                      | $6.9 \times 10^{-5}$                      | 0,73                   | 146                     |
| G4     | –                    | 10.4         | 8     | 0 | 46.3     | 15.4          | NP-IL      | 5                       | $2.2 \times 10^{-4}$                      | 0,83                   | 466                     |
| G5     | –                    | 10.4         | 8     | 0 | 43.5     | 14.6          | NP-IL      | 10                      | $1.2 \times 10^{-4}$                      | 0,86                   | 437                     |
| G6     | –                    | 10.4         | 8     | 0 | 41.4     | 13.8          | NP-IL      | 15                      | $8.7 \times 10^{-5}$                      | 0,9                    | 386                     |
| G7     | –                    | 10.4         | 8     | 0 | 46.3     | 15.4          | NP-UPy     | 1                       | $1.3 \times 10^{-4}$                      | 0,87                   | 483                     |
| G8     | –                    | 10.4         | 8     | 0 | 43.5     | 14.6          | NP-UPy     | 5                       | $1.8 \times 10^{-4}$                      | 0,85                   | 424                     |

Our approach focused on introducing nanofillers while maintaining the other components constant, to understand the effect of nanoparticle incorporation prior to further optimization. The prepared compositions are summarized in Table 1. G1 serves as the reference sample, containing the covalent crosslinker but no nanofillers. Formulations incorporating 5 and 10 wt% of NP-IL (G2 and G3, respectively) exhibited a reduction in ionic conductivity from  $1.1 \times 10^{-4} S\text{ cm}^{-1}$  (G1) to  $9.5 \times 10^{-5} S\text{ cm}^{-1}$  (G2) and  $6.9 \times 10^{-5} S\text{ cm}^{-1}$  (G3) at room temperature. Although NP-IL possesses abundant ionic liquid moieties on its surface, its presence likely restricts the mobility of the polymer chains and decreases overall ionic conductivity. A similar trend was observed in mechanical testing (Fig. 4A): the reference gel G1 showed the highest elongation at break, whereas G2 and G3 fractured at lower elongations. Subsequently, we prepared gel formulations without covalent crosslinkers but with additional nanofillers (keeping the molar ratio of M-IL and M-UPy constant). A comparison between G2 (containing a covalent crosslinker) and its counterpart G4 (without the covalent crosslinker) revealed a significant improvement in mechanical flexibility. Elongation at break increased from 146% (G2) to 466% (G4) - a more than threefold enhancement (Fig. 4B). Additionally, the tensile strength rose from 0.58 MPa to 0.83 MPa, indicating that the nanofillers contributed to reinforcement of the polymer network. Further increasing the NP-IL content slightly reduced the elongation at break to 386% (G6), suggesting that excessive filler loading may lead to reduced chain mobility.

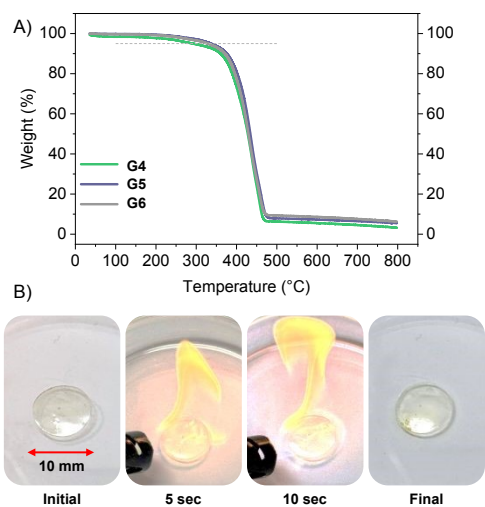
A similar behavior was observed for composites containing NP-UPy (Fig. 4C). However, the incorporation of NP-UPy was limited to below 5 wt% as higher contents led to reduced dispersivity forming non-transparent samples. This is presumably due to strong interparticle interactions, which promote aggregation. In contrast, NP-IL could be incorporated

at higher concentrations as a result of improved dispersibility by IL-functionalized surface (better chemical compatibility with the ionic liquid-based polymer matrix). The ionic conductivity of the gel composites was characterized using broadband dielectric spectroscopy (BDS) over a temperature range of  $-20$  to  $70\text{ }^{\circ}\text{C}$  (see ESI, Figures S11–S18). In a typical measurement, the dielectric response was recorded across a frequency range of  $10\text{--}10^7$  Hz. The resulting frequency-dependent conductivity curves (Fig. 4D) exhibit a distinct plateau region at each temperature, from which the DC conductivity values were extracted. Significant increase in conductivity was observed with increasing temperatures as expected. The temperature-dependent conductivity plots for the gel composites (Fig. 4E) display a nonlinear relationship, characteristic of polymer-based electrolytes. This behavior follows the Vogel–Tammann–Fulcher (VTF) model (ESI, Figure S3),<sup>44, 45</sup> which describes ion transport in polymeric systems and reflects the dynamic nature of the gel matrices. Among the studied samples, G4 exhibited the highest conductivity values across the entire temperature range. With the incorporation of only 5 wt% NP-IL, G4 achieved a maximum conductivity of  $2.7\text{ mS cm}^{-1}$  at  $70\text{ }^{\circ}\text{C}$ . A comparison between G4 and G2 indicates that the removal of the covalent crosslinker and the addition of NP-ILs resulted in a more than two-fold improvement in conductivity across all temperatures (Fig. 4F). Furthermore, the ionic conductivity of the gel composites was evaluated after 12 months of storage in a glove box and showed no significant change compared to the pristine material, confirming the good long-term stability of the prepared gel composites (ESI, Figure S23).





**Fig. 4.** Stress-strain curves of PIL gel composites (strain rate of  $20 \text{ mm}\cdot\text{min}^{-1}$ ): A) G1-G3, B) G2, G4-G6, C) G2, G7 and G8; D) Frequency dependent conductivity in the temperature range of  $-20$  to  $70$  °C with  $10$  °C increments, conductivity as a function of inverse temperature for E) G4-G8 and F) G4 vs G2



**Fig. 5.** A) Thermogravimetric analysis of G4-G6 and B) flammability test of gel composite.

In addition to ionic conductivity, the thermal and safety properties of the polymer electrolytes were evaluated. Thermogravimetric analysis (Fig. 5A) confirmed that the composites exhibited excellent thermal stability, with no significant weight loss up to  $330$  °C for **NP-IL**-containing formulations. In contrast, systems utilizing **NP-UPy** particles showed degradation onset above  $250$  °C, indicating a lower thermal stability limit for those materials. Another critical parameter for electrolyte safety is flammability. As shown in Fig. 5B, the gel composites are entirely flame retardant. In a simple test, a direct flame was applied to the specimen for 10 seconds. The material neither ignited nor exhibited any visible

degradation. These observations were further confirmed by UL 94 flammability tests, in which material achieved a V-0 grading for a thickness of  $1$  mm (see ESI, Table S1, Figure S22), demonstrating its excellent flame retardant and suitability for safe electrochemical applications.

The introduction of additional dynamic interactions (ionic interactions derived from **NP-IL** and supramolecular hydrogen-bonding interactions contributed by **NP-UPy**) was expected to enhance the reprocessability of the gel composites. To evaluate this, broken gel fragments were placed into a mold and reprocessed using a hot-vacuum press at  $120$  °C for 3 hours. The results of this procedure are presented in Fig. 6A. Regardless of the type or amount of additional fillers, all composites exhibited complete recovery of their macroscopic shape, forming transparent, self-standing films after reprocessing. However, subsequent drying at  $120$  °C under vacuum for eliminating any residual moisture, affected the dimensional stability. Gels containing higher contents of **NP-IL** demonstrated superior shape retention and structural integrity after drying, while those with lower **NP-IL** or **NP-UPy** content displayed noticeable deformation or shrinkage. To further verify the effectiveness of reprocessing process, broadband dielectric spectroscopy measurements were performed on the reprocessed gels. As shown in Fig. 6B, the temperature-dependent conductivity of the reprocessed **G6** sample nearly overlapped with the pristine material, indicating that the ionic transport characteristics were fully restored. Thus, the dynamic crosslinking interactions enabled efficient reformation of the gel network without significant loss of electrochemical performance.



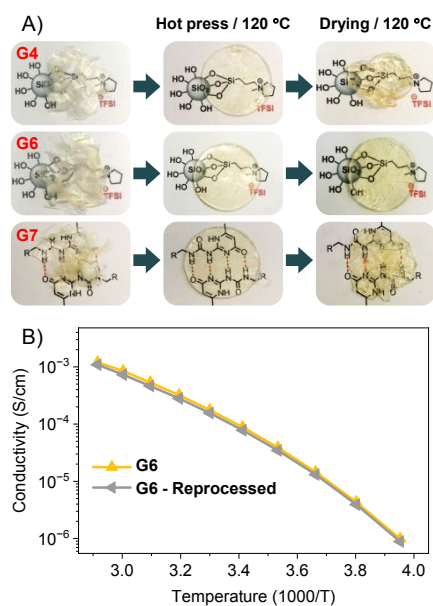


Fig. 6. A) Reprocessing of G4, G6 and G7 via hot-press at 120 °C for 3 hours; B) conductivity as the function of temperature of G6 before and after reprocessing.

## Conclusions

PIL-based gel composites were successfully prepared by incorporating surface-modified silica nanoparticles functionalized with either ionic liquid or ureidopyrimidinone groups. The covalent attachment of functional moieties to the nanoparticle surfaces was confirmed through various characterization techniques, including solid-state CP MAS <sup>29</sup>Si NMR spectroscopy, FT-IR, and thermogravimetric analysis. The introduction of these surface -modified nanoparticles significantly enhanced the dynamic behavior of the resulting gel composite systems. Specifically, samples demonstrated improved reprocessability and remarkable mechanical flexibility, achieving elongations at break of up to 460%. Notably, these mechanical properties were reached solely through dynamic interactions, without the need for permanent covalent crosslinking. Furthermore, reprocessing of composites displayed high efficiency, completely recovering ionic conductivity. The gels additionally exhibited excellent ionic transport characteristics across a broad temperature range, achieving a conductivity of  $2.2 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature. The materials displayed outstanding thermal stability, with decomposition temperatures up to 330 °C and were inherently flame retardant, showing their potential for safe and durable applications in electrochemical and flexible devices. This now allows the gel to be reshaped, repaired, or fully reprocessed without significant loss of performance. For recovery from used batteries, the battery would first undergo standard disassembly procedures, including removal of the casing, current collectors, and electrode stacks. Since the gel electrolyte is typically located within the separator or at the electrode–electrolyte interface, the electrode layers can be carefully separated mechanically. Through controlled solvent treatment or thermal activation of the dynamic bonds, the gel

electrolyte can be detached from the electrodes and reprocessed into a new film or reshaped for reuse.

## Author contributions

Conceptualization, A. M., Z. K. and W. H. B.; data curation, H. H., T. L. T., R. G. S. and Z. K.; formal analysis, H. H., R. G. S. and Z. K.; funding acquisition, A. M. and W. H. B.; investigation, H. H., T. L. T., R. G. S., S. K., H. R., A. M., Z. K.; methodology, A. M., Z. K. and W. H. B.; project administration, A. M., Z. K. and W. H. B.; resources, A. M., Z. K. and W. H. B.; supervision, A. M., Z. K. and W. H. B.; validation, H. H., T. L. T., R. G. S. and Z. K.; visualization, H. H. and Z. K.; writing—original draft preparation, H. H., A. M., Z. K. and W. H. B.; writing—review and editing, H. H., A. M., Z. K. and W. H. B.; All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

“There are no conflicts to declare”.

## Data availability

All original data are stored in our electronic labnotebook (E-lab), where the original data can be retrieved on demand. Organization of these data inside the system is according to the rules of the DFG (German Research Foundation). This access can be granted on request, but cannot be provided by an open link, to secure other data inside the system. We provide all data on <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, Tensile Testing, CP-MAS, TGA, FT-IR, TEM and BDS electronically on demand.

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## Data availability

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