

LiZnSO₄F Made in an Ionic Liquid: A Ceramic Electrolyte Composite for Solid-State Lithium Batteries

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The search for good solid electrolytes constitutes a major goal towards the development of safer lithium batteries. A few candidates do exist, but they suffer either from narrow electrochemical window stability or too low ionic conductivity. Herein we report the ionic-liquid-assisted synthesis of a novel LiZnSO₄F fluorosulfate phase having a sillimanite LiTiOPO₄-type structure, which on simply pressed samples shows a room-temperature ionic conductivity of 10^{-5} – 10^{-7} S cm⁻¹ together with a 0–5 V electrochemical stability window range, while ionic-liquid-free LiZnSO₄F shows an ionic conductivity four orders of magnitude lower (10^{-11} S cm⁻¹). While robustly reproducible but not yet fully understood, this finding offers new opportunities to tailor inorganic composites with higher ionic conductivity. The origin of such results is demonstrated to be rooted in a surface effect associated with the grafting of a lithium-containing ionic liquid layer. This finding opens up new opportunities for the design of ceramic composites with higher ionic conductivity and should serve as an impetus for further exploiting the chemistry of ionic liquid grafting on oxides.

Renewable energy sources and electric automotive transportation are popular topics in today's energy-conscious society, hence placing rechargeable batteries as one of the major technological sciences in this new century.^[1] Advances in energy storage are a tribute to chemists' abilities to design new and better materials. In the hunt for novel electrode materials, notions of sustainability must be considered.^[2] This is the reason why LiFePO₄, which is made of inexpensive and abundant chemical elements, has attracted the attention of the research community despite its poor conducting properties. By particle downsizing and carbon nanocoating, LiFePO₄/C composite overcomes transport limitations and is capable of reversibly and rapidly intercalating 0.9 Li

(ca. 160 mA h g⁻¹) at a redox voltage of 3.43 V versus Li. Thus, it has become one of the most praised electrode materials for the next generation of rechargeable batteries for high-volume applications.^[3]

Further exploring the chemistry of polyanionic-based insertion electrodes, we recently synthesized, by an ionothermal process, a novel 3.6 V LiFeSO₄F electrode showing a reversible capacity nearing 140 mA h g⁻¹ (theoretical capacity = 151 mA h g⁻¹), good rate capability, and cycling stability.^[4] This fluorosulfate was found to crystallize in a favorite structure (space group *P* $\bar{1}$) with three-dimensional channels for Li diffusion as opposed to the one-dimensional channels in LiFePO₄. Most likely, from the 3D versus 1D change in the conduction path, the use of LiFeSO₄F powders will obviate the need for nanosizing or carbon coating, while the same cost and environmental advantages are maintained.

Since our early report, we have considerably enlarged the fluorosulfate family with the discovery of AMSO₄F (A = Li, Na and M = Co, Ni, Mn, etc.) homologues.^[5] This new family of materials, practically unknown a year ago, counts no less than 20 members showing related structures with either promising electrochemical or attractive ionic properties. Among them, the sodium-based 3d-metal fluorosulfates, which crystallize in a titanite structure (derived from the favorite structure, space group *P*2₁/*c*) and have localized positions for the Na⁺ ions, were found to show a four-fold increase in ionic conductivity as compared to their Li-based counterparts on cold-pressed powders (10^{-7} S cm⁻¹ for Na vs. 10^{-11} S cm⁻¹ for Li at room temperature). While far from the hallmark solid-state electrolytes for future Li batteries such as Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAG), Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LAT), and Li_{3+x}PO_{4-x}N_x (LIPON), which have room-temperature conductivities of 2.8×10^{-4} S cm⁻¹, 10^{-3} S cm⁻¹, and 10^{-6} S cm⁻¹, respectively, such a finding was an impetus to look for further fluorosulfate members as part of the effort to develop new ceramic electrolyte materials with increased conductivity, thus allowing a switch from thin-film to bulk technology in all solid-state batteries.^[6]

Besides high ionic conductivity, a pivotal figure of merit for solid-state electrolytes is the width of their electrochemical stability window. This window is limited for ionic conducting ceramics containing 3d-metal elements, such as Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃, owing to the reduction of Ti⁴⁺ in Ti³⁺ at approximately 2.4 V. So our strategy was to search for other members of the fluorosulfate AMSO₄F family containing divalent metals that cannot be easily reduced or oxidized. Besides LiMgSO₄F, the first reported fluorosulfate,^[7] other attractive candidates could enlist lead, tin, or zinc to prepare AMSO₄F phases. Mindful of the previously reported struc-

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tural affiliation between the precursor $\text{MSO}_4 \cdot \text{H}_2\text{O}$ and the product AMSO_4F phase, we searched for $\text{MSO}_4 \cdot \text{H}_2\text{O}$ phases ($\text{M} = \text{Zn}$, Pb , and Sn) having the same structure as $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. We identified $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ to be isostructural with $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. Thus, we prepared the $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ precursor either by using the ionic liquid (IL) 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI) or by a ceramic route and later treated it with a stoichiometric amount of LiF at 300°C by either ionothermal or solid-state (ceramic) synthesis. We succeeded in preparing the LiZnSO_4F phase involving a topotactic reaction; the structural and transport properties of this phase are reported. Depending upon the IL or ceramic-based precursors, the final products are henceforth named $\text{LiZnSO}_4\text{F-IL}$ or $\text{LiZnSO}_4\text{F-C}$, respectively. We found that LiZnSO_4F does not crystallize into a tavorite (triclinic) structure but instead favors a sillimanite (orthorhombic) structure and shows a room-temperature ionic conductivity of 10^{-5} – $10^{-7} \text{ S cm}^{-1}$.

The crystal structure of LiZnSO_4F was solved from synchrotron data by Rietveld refinement using the FullProf program.^[8] Isostructural with the sillimanite LiTiOPO_4 structure (Figure 1a),^[9] LiZnSO_4F crystallizes into an orthorhombic cell (space group: $Pnma$) with the cell parameters $a = 7.40357(9) \text{ \AA}$, $b = 6.32995(7) \text{ \AA}$, $c = 7.42016(9) \text{ \AA}$ and $V = 347.740(7) \text{ \AA}^3$. All crystallographic data as well as agreement factors are summarized in Table 1 (corrected for background). The high χ^2 value mainly reflects the extremely high counting statistics of the powder diffraction data obtained from a 2D detector. The structure (Figure 1b) is built up from SO_4 tetrahedra and zinc-centered ZnO_4F_2 octahedra. The latter are linked together through fluorine atoms (in *trans* positions), thus creating chains along the a axis. These chains are interconnected by SO_4 tetrahedra. Indeed, each SO_4 tetrahedron shares two of its vertices with two ZnO_4F_2 octahedra from a first chain, while the two remaining vertices are linked to two other ZnO_4F_2 chains (see the Supporting Information). This arrangement leads to the formation of tunnels along the a axis (Figure 1b) that host Li atoms.

The ionic conductivity was measured with ionically blocking electrodes for $\text{LiZnSO}_4\text{F-IL}$ pressed pellets. Typical impedance spectra (a small semicircle along with a large Warburg diffusion tail) suggest a very high ionic mobility. Ionic conductivity values as high as $2.8 \times 10^{-5} \text{ S cm}^{-1}$ were repeatedly recorded at room temperature for several samples (Figure 2a); these values were six orders of magnitude higher than for the tavorite LiFeSO_4F compound. This manifold increase in conductivity can be due either to the crystal structure or to the surface modification in LiZnSO_4F (e.g. onset of grain boundaries).

Taking advantage of the non-paramagnetic Zn center, we performed a solid-state NMR spectroscopy (^{19}F , ^1H , and ^7Li) study, which captured the narrow ^1H and ^{19}F signals arising from the EMI-TFSI ionic liquid (Figure 3). The ^1H NMR spectrum of $\text{LiZnSO}_4\text{F-IL}$ features the five peaks characteristic of the EMI cation. Moreover, their positions are shifted by $\delta = -1.5 \text{ ppm}$ (Figure 3c) as compared to free EMI-TFSI, probably because of the change in magnetic susceptibility at the $\text{LiZnSO}_4\text{F-IL}$ surface.^[10] Besides, the ^{19}F NMR spectrum

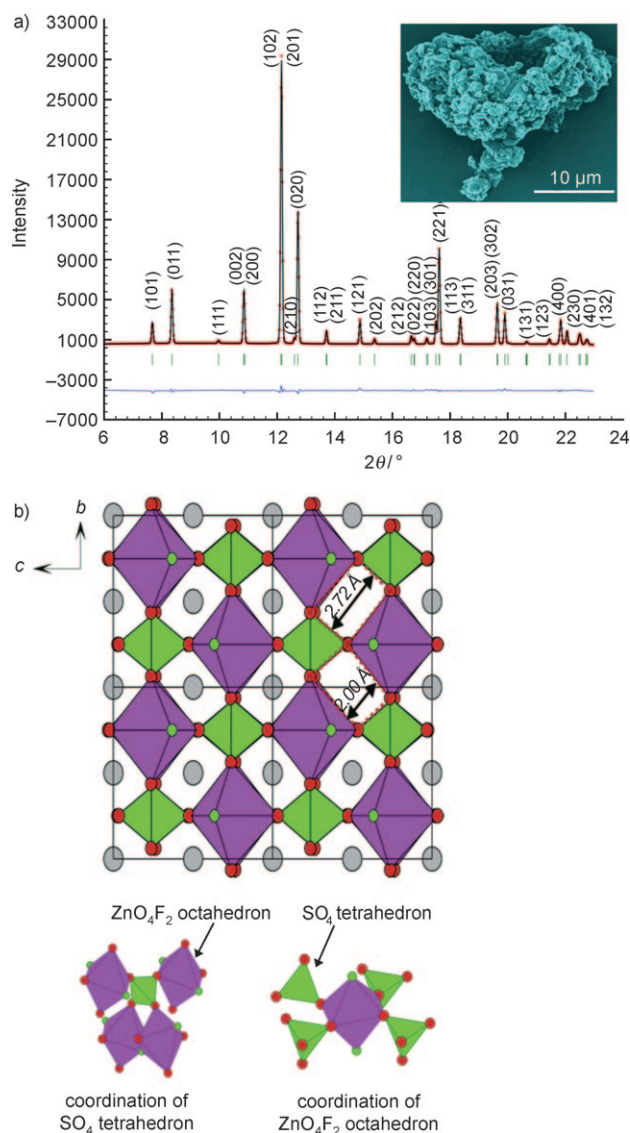


Figure 1. a) Synchrotron XRD pattern ($\lambda = 0.701277 \text{ \AA}$) of single-phase LiZnSO_4F . The red dots are the experimental diffraction pattern, the black line is the simulated pattern, the green ticks are the Bragg peak positions, and the blue line is the difference between the experimental and the simulated pattern. The inset shows a representative SEM image with a particle size range of 800–1200 nm. b) The sillimanite structure of LiZnSO_4F showing the interconnected ZnO_4F_2 octahedra (pink), SO_4 tetrahedra (green), and Li atoms. Li gray, O red, F green. The local coordination of a SO_4 tetrahedron and a ZnO_4F_2 octahedron is also shown. Further structural images are shown in the Supporting Information.

reveals three distinct signals, one narrow (e.g. mobile) signal corresponding to the trifluoromethyl groups from TFSI, another broader, intense signal from F within the crystallized LiZnSO_4F structure, and the third corresponding to F from LiF. Interestingly, the ^{19}F signals coming from the IL and LiF are amplitude-correlated. From these NMR spectroscopy measurements, we estimate the ionic liquid monolayer trapped at the surface of the LiZnSO_4F particles to range from 8–15 nm, assuming particles having an average diameter of 0.5–1 μm . The presence of ionic liquid in the final samples

Table 1: Lattice parameters, cell volume, and atomic coordinates for LiZnSO_4F with orthorhombic ($Pnma$) symmetry.

LiZnSO_4F	a [Å]	b [Å]	c [Å]	Volume [Å ³]
	7.40357(9)	6.32995(7)	7.42016(9)	347.740(7)
α	β	γ		
90°	90°	90°		
χ^2	R_p	R_{wp}	R_{Bragg}	
1730	3.26	3.48	0.88	
Atom	Wyckoff position	x	y	z
Li	4a	0	0	0
Zn	4c	0.14345(18)	$\frac{1}{4}$	0.29262(14)
F	4c	0.4011(7)	$\frac{1}{4}$	0.3660(3)
S	4c	0.3623(4)	$\frac{1}{4}$	0.8589(3)
O1	8d	0.1270(5)	0.5625(4)	0.2352(3)
O2	4c	0.2033(7)	$\frac{1}{4}$	−0.0239(5)
O3	4c	0.0298(8)	$\frac{1}{4}$	0.5380(5)

was also assessed by FTIR spectroscopy and X-ray photoelectron spectroscopy (XPS, see the Supporting Information). Traces of ionic liquid come from the IL-assisted synthesis of the $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ precursor, which can modify LiZnSO_4F grain boundaries by surface coating and consequently affects its ionic conductivity.

To check this assumption, we washed the $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ precursor with ethyl acetate several times to remove any IL contamination. Consequently, the ionic conductivity dropped to approximately $10^{-7} \text{ S cm}^{-1}$ at room temperature after two thorough washing steps and remained constant whatever the number of subsequent washings (Figure 2a). Furthermore, we prepared $\text{LiZnSO}_4\text{F-C}$ products from an ionic-liquid-free $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ precursor (e.g. obtained from a vacuum temperature-driven process). This material bears the same X-ray pattern and crystal structure as those made by the IL route and, as expected, its ^{19}F NMR spectra does not show any peaks corresponding to TFSI (Figure 3). It exhibits an ionic conductivity of approximately $10^{-11} \text{ S cm}^{-1}$, which is similar to the conductivity of the parent LiFeSO_4F fluorosulfate phase. Interestingly, the ionic conductivity of the $\text{LiZnSO}_4\text{F-IL}$ samples remains the same (ca. $10^{-7} \text{ S cm}^{-1}$) whatever the number of washing steps in ethyl acetate, implying that 1) the $\text{LiZnSO}_4\text{F-IL}$ grains are covered with an ionic liquid layer strongly interacting with the grain surface and 2) the ionic liquid “contamination” of the precursor $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ phase is crucial in controlling the ionic conductivity of the $\text{LiZnSO}_4\text{F-IL}$ compounds. Last, it should be mentioned that annealing the $\text{LiZnSO}_4\text{F-C}$ in ionic liquid at 280°C for 24 h does not affect its ionic conductivity (ca. $10^{-11} \text{ S cm}^{-1}$). For each reported data value, measurements were repeated three times, and inherent errors were small ($\pm 0.3 \times 10^{-6} \text{ S cm}^{-1}$), giving us confidence that our observed trends are robust.

DC polarization measurements on ionic-liquid as well as ceramic-precursor-based LiZnSO_4F were performed on symmetric $\text{Li} | \text{PEO-LiClO}_4 | \text{LiZnSO}_4\text{F} | \text{PEO-LiClO}_4 | \text{Li}$ cells at 70°C . The possibility of measuring currents (Figure 2b) implies first the existence of Li^+ mobility within LiZnSO_4F . Secondly, the markedly higher current measured for $\text{LiZnSO}_4\text{F-IL}$ than for $\text{LiZnSO}_4\text{F-C}$ is fully consistent with our

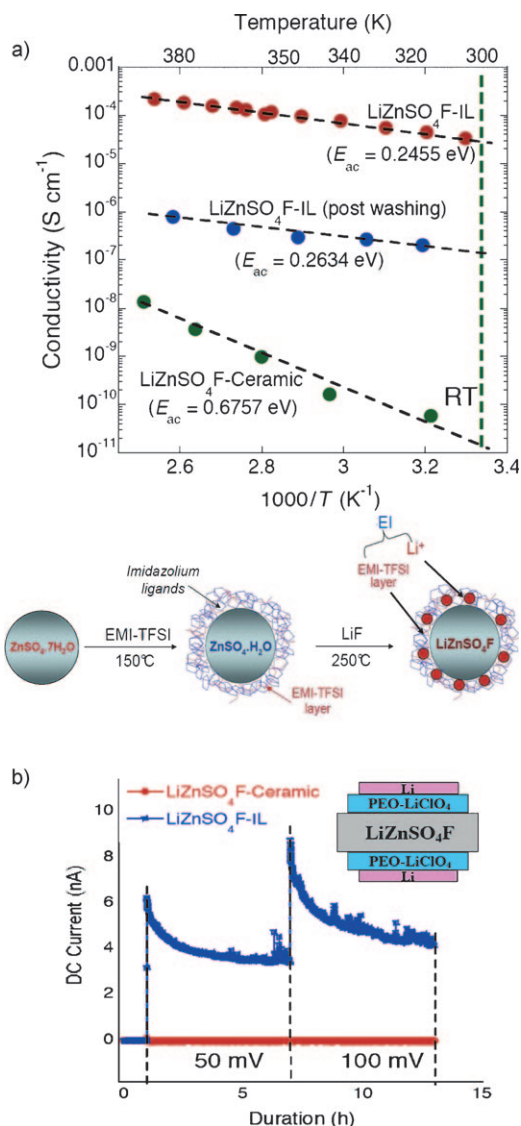


Figure 2. a) AC conductivity of ionic blocking LiZnSO_4F pellets prepared using $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ precursor made with and without ionic liquid. The presence of a thin layer of ionic liquid (from the precursor) leads to a very high Li -ion room-temperature conductivity of approximately $10^{-5} \text{ S cm}^{-1}$. Even after multiple washings of the sample with ethyl acetate, a permanent layer of ionic liquid remains on LiZnSO_4F , giving a high conductivity of about $10^{-7} \text{ S cm}^{-1}$. A schematic depiction of the ionic conductivity enhancement caused by the capture of ionic liquid layer around the particles is given (bottom). The “ceramic” LiZnSO_4F sample, on the other hand, gives a very low conductivity of approximately $10^{-11} \text{ S cm}^{-1}$. The activation energy values (E_{ac}) are provided. b) Polarization current measurement of LiZnSO_4F pellets with and without ionic liquid in a Swagelok cell with $\text{Li} | \text{PEO} | \text{LiZnSO}_4\text{F} | \text{PEO} | \text{Li}$ configuration (inset; PEO = poly(ethylene oxide)). The current solely involves Li^+ ion mobility through the LiZnSO_4F pellet, thus showing that it is a Li^+ ion conductor. The presence of ionic liquid favors higher Li^+ ion conductivity.

conductivity measurements, which reveal the same trend. The steady-state current at times beyond the establishment of a concentration gradient in the PEO films with this setup is related to the lithium-ion conductivity. Indeed, the $\text{Li} | \text{PEO-LiClO}_4$ interface is only reversible for lithium (in the absence

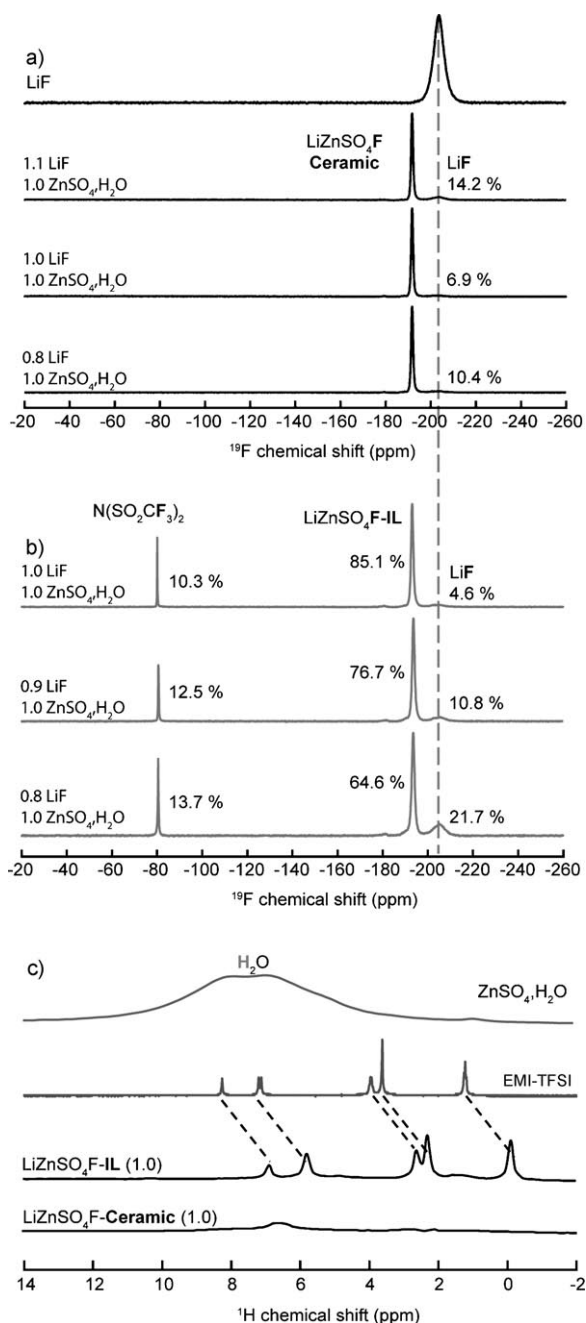


Figure 3. a) ^{19}F NMR spectra of LiF and LiZnSO₄F ceramic prepared with 1.1, 1.0, and 0.8 mol of LiF per 1.0 mol ZnSO₄·H₂O. b) ^{19}F NMR spectra of LiZnSO₄F-IL samples with different LiF/ZnSO₄·H₂O ratios, featuring an additional peak corresponding to the CF₃ group of TFSI at $\delta = -80$ ppm. c) ^1H NMR spectrum of IL-free ZnSO₄·H₂O and pure EMI-TFSI compared with LiZnSO₄F-IL showing a $\delta = -1.5$ ppm shift between the two spectra, and LiZnSO₄F ceramic.

of any side reaction), and PEO-LiClO₄ is an electronic insulator.

Both impedance and DC polarization measurements jointly confirm a greater ionic conductivity for the ionic-liquid-made LiZnSO₄F samples as compared to the ceramic ones and by the same token highlight the positive role of the ionic liquid treatment in improving the ionic conductivity of

LiZnSO₄F. At first, we might hypothesize that such an ionic conductivity results from an encapsulation of the LiZnSO₄F grains by a layer of ionic liquid that provides the proper percolation network for ionic conduction. Nevertheless, it remains crucial to understand the underlying mechanism underpinning such a finding.

We should recall that ionic liquids are good ionic conductors, with conductivities of approximately 10^{-2} S cm⁻¹ for EMI-TFSI. So the high ionic conductivities (ca. 10^{-5} – 10^{-7} S cm⁻¹) measured for LiZnSO₄F-IL samples could simply be due to the ionic liquid layers forming a percolating path around the LiZnSO₄F. Such a picture, however, is not correct, as it does not take into account the DC polarization measurements, which imply a Li⁺ ionic conduction. Moreover, we have shown that $\log \sigma = f(1/T)$ for LiZnSO₄F nicely follows an Arrhenius law, thus implying that the measured ionic conductivity is not dictated entirely by the ionic liquid, as the temperature dependence of ionic conductivity for the latter follows a Vogel–Tamman–Fulcher (VTF) law. However, the above AC and DC measurements can be reconciled by assuming that the ionic liquid layers will solvate Li⁺ ions; this hypothesis is well supported by the existence of 1M LiX solutions in EMI-TFSI electrolytes (X⁻ = PF₆⁻, TFSI⁻, etc.). The TFSI anion, though weakly coordinating, is able to solvate lithium.^[11] So the observed IL-driven ionic conductivity increase for the LiZnSO₄F-IL samples is most likely due to a Li-bearing ionic liquid layer grafted onto the surface of the LiZnSO₄F particles (Figure 2a). Such a surface effect does not come as a total surprise as there is past and recent evidence showing the feasibility 1) of apparently enhancing bulk conductivity by creating fast ion-conduction surfaces through controlled adjustment of stoichiometry^[12] or 2) of using hybrid ionic-liquid-tethered nanoparticle materials doped with LiTFSI as electrolytes for Li batteries.^[13,14] It now remains to be explained by which process some ionic liquid layers remain trapped at the surface of the particle and how they could affect the resulting sample ionic conductivity.

Our synthesis experiments clearly imply that the ionic liquid capturing step occurs during the formation of ZnSO₄·H₂O precursor from ZnSO₄·7H₂O in ionic liquid medium, as LiZnSO₄F ceramic samples annealed at 280 °C in ionic liquid were shown (as deduced from IR measurements) to be IL-free. Such a dehydration process, which involves the departure of water in a hydrophobic ionic liquid medium, leads to an interfacial H₂O/ionic liquid medium which, by virtue of a yet unknown mechanism, leads to the fixation of an ionic liquid layer at the surface of the ZnSO₄·H₂O material. The reaction of ZnSO₄·H₂O with LiF to give LiZnSO₄F is topotactic, and so it does not come as a surprise that this electrolyte-type layer is preserved in the final LiZnSO₄F phase. Now regarding the nature of the IL–LiZnSO₄F interactions, both XPS and NMR measurements suggest a different chemical environment in this layer, with a noticeable shift ($\delta = -1.5$ ppm) observed for the five peaks of the EMI cations in the ^1H NMR spectrum. Such a shift is most likely rooted in the proximity of the LiZnSO₄F surface, which additionally gives rise to relatively narrow lines for solid-state NMR spectra of ^1H (e.g. compared to the H₂O resonance in ZnSO₄·H₂O), thus indicating that the EMI-TFSI ions remain

quite mobile even if they are trapped onto the LiZnSO_4F -IL surface.

Turning to the enhanced lithium-ion conductivity, we can infer several possibilities such as 1) an increased LiF surface solubility, owing to the well-known fact that dielectric constants can easily be enhanced at truncated surfaces, and 2) an IL-driven enhanced disproportionate process that will facilitate the surface Li displacement. Although we cannot ascertain whether both effects take place simultaneously, we favor the latter as it is more consistent with the correlation in the NMR spectroscopy signal amplitude between the IL and LiF signals, which is also observed for samples purposely prepared with LiF deficiency. It is worth mentioning that such an ionic conductivity difference between ceramic- and ionic-liquid-made fluorosulfates is not general, as the ionic conductivity of LiFeSO_4F was found to be $10^{-11} \text{ S cm}^{-1}$ irrespective of the synthesis route. Such different behavior between $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot\text{H}_2\text{O}$ precursors with respect to ionic-liquid trapping is mostly related to differences in their chemistry, as already witnessed by the observed structural differences. Surface properties involving wettability, catalytic properties, or chemical reactivity are well known to be ruled out by the bulk crystal symmetry, with enhanced properties associated with the way that the surface is truncated along specific crystallographic directions. On that basis, the greater aptitude of the $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ phase towards capturing an ionic liquid monolayer at its surface is not a total surprise.

Overall, our LiZnSO_4F -IL can simply be viewed as a composite electrolyte formed of LiZnSO_4F grains surrounded by a conducting lithium-containing ionic liquid layer (e.g. electrolyte interface, Figure 2a), while the exact nature of the interface remains unclear. Future work will prioritize determining the exact nature of the ionic liquid/ LiZnSO_4F surface by a variety of analytical techniques coupled with the development of chemical approaches to purposely graft ionic liquids on various surfaces. Although we have not yet elucidated the exact mechanism, we provide direct experimental evidence that ceramic powders “functionalized” with ionic liquids could provide a versatile route to turn disregarded Li-based ionic conductors into attractive solid electrolytes. This claim can only be supported by the recent achievement of extremely high conductivity in nanocomposite electrolytes based on LiF-functionalized titania plasticized with EMI-TFSI ionic liquid.^[15] Although the presently achieved ionic conductivities in the range of $10^{-5} \text{ S cm}^{-1}$ are still too low for developing practical solid-state lithium batteries, there is room for improvement owing to the rich ionic liquid chemistry.^[14] We thus believe that composites of ceramics and ionic liquids as solid electrolytes could have a bright future in the field of energy storage.

Experimental Section

Synthesis: First, $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ monohydrate precursor was prepared by annealing commercial $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ (Aldrich, 99 %), either immersed in EMI-TFSI ionic liquid or in primary vacuum at 150°C for 1 h to remove excess structural water, washing the resulting powder with dichloromethane/ethyl acetate, and drying at 60°C . Then, LiZnSO_4F was synthesized through ionothermal synthesis by 1) mixing

$\text{ZnSO}_4\cdot\text{H}_2\text{O}$ and LiF (in 1:1 molar ratio) in EMI-TFSI ionic liquid (3 mL) medium inside a Teflon-lined Parr bomb, 2) stirring the mixture for 5 min, and 3) heating the Parr bomb in an oven to 300°C for 5 h (heating rate 2°C min^{-1}). Upon cooling to ambient temperature, the reaction product was recovered by washing with dichloromethane, centrifuging, and drying the white powder at 60°C . Alternately, LiZnSO_4F can be synthesized by a solid-state route by mixing $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ with LiF (in 1:1 molar ratio) by ball-milling for 5 min, making a pellet using a uniaxial press (10 bar), heating the pellet inside a Teflon-lined Parr bomb reactor at 300°C for 30–40 h (heating rate 2°C min^{-1}) involving an autogeneous pressure (3 bar) before cooling it to room temperature to obtain the final product.

Characterization: X-ray diffraction patterns were collected on a Bruker D8-Advantage powder diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda_1 = 1.54053 \text{ \AA}$, $\lambda_2 = 1.54431 \text{ \AA}$) equipped with a LynxEye detector (operating at 40 kV, 40 mA). Synchrotron powder diffraction data were collected in the Swiss–Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The sample was poured into a thin-walled glass capillary of 0.5 mm o.d. and measured at 295.0 K. The temperature was controlled with an Oxford Cryostream 700+ instrument. The data were collected using a MAR345 image plate detector at a sample-to-detector distances of 150, 250, and 400 mm, in order to combine high structural and angular resolutions, and a selected X-ray wavelength of $\lambda = 0.701277 \text{ \AA}$. The beam was slit to $300 \times 300 \text{ }\mu\text{m}$. The capillary was oscillated by 30° during an exposure to the X-ray beam for 30 s. After the measurements at room temperature, the sample was studied in the 80–500 K range. For that it was cooled to 80 K and then heated from up to 500°C at a rate of 1 K min^{-1} while the diffraction patterns were collected. One pattern was recorded every 2 min (2 K steps), making a total of 212 patterns for the 80–500 K temperature scan. All of the obtained raw images were transformed into 1D powder patterns using the FIT2D program^[16] and calibration measurements of the standard NIST LaB_6 sample. Uncertainties of the integrated intensities were calculated at each 2θ point by applying Poisson statistics to the intensity data and considering the geometry of the detector. The powder patterns were indexed using DICVOL,^[17] and the complete structure was refined by Rietveld refinement using the FullProf program.^[8] A total of 30 parameters has been used for the refinement in the following order: 1 for the scale, 3 for the cell parameters, 1 for the zero shift, 5 for the profile (pseudo-Voigt peak profile), 13 for the atomic positions, and finally 7 for the isotropic atomic displacement factors. Thermogravimetric analysis was conducted between 30 and ca. 800°C (heating rate $10^\circ\text{C min}^{-1}$, in air) using a Simultaneous Thermal Analyzer STA 449C Jupiter unit (Netzsch Inc). SEM microscopy images were obtained using an FEI Quanta 200 F field-emission scanning electron microscope (20 kV) operating under low vacuum to avoid any charging effects. Elemental analysis was performed at several spots to ensure homogeneous distribution of all elements. TEM microscopy images were obtained using an FEI Tecnai F20 S-Twin electron microscope (200 kV) on the powder sample deposited on a TEM holey (with carbon–copper) grid.

All NMR spectroscopy experiments were performed on a 7 T Bruker Avance NMR spectrometer (300 MHz for ^1H , 282 MHz for ^{19}F , and 117 MHz for ^7Li) using a 1.3 mm double-resonance probe for ^1H and ^{19}F operating at 60 kHz MAS and a 4 mm double-resonance probe for ^7Li operating at 14 kHz. Recycling delays for ^1H and ^{19}F were set to 120 s and four transients were recorded, using 150 and 200 kHz B^1 fields for excitation. The recycling delay was set to 1 s and 16 transients were recorded for ^7Li with a $1.1 \text{ }\mu\text{s}$ long $\pi/12$ excitation pulse. The chemical shifts were referenced with 4-acetophenone at $\delta = -107 \text{ ppm}$ for ^{19}F and TMS at 0 ppm for ^1H . The peak relative intensities were calculated using the dmfit software.^[18]

Conductivity measurements: LiZnSO_4F powder was pressed first by uniaxial press (10 bar) followed by isostatic press (2500 bar) to form a dense pellet 12 mm in diameter and 1–2 mm in thickness (75 % theoretical density). Ionically blocking electrodes were made by

sputtering gold on both faces of the pellet. AC and DC conductivity studies were performed by employing (AC) impedance spectroscopy (200 kHz–10 MHz) and 1–2 V DC polarization, respectively. Varying the temperature from room temperature to 140°C, the conductivity data were recorded using a Bio-logic VMP3 instrument. Activation energies E_a for AC and DC conductivities were calculated by the Arrhenius relation $\log(\delta T) = \log(\delta_0 T_0) - E_a/k_B T$ (where δ = conductivity in Scm^{-1} , T = temperature, and k_B = Boltzman constant). Furthermore, polarization measurements (Li mobility) on a LiZnSO_4F pellet were performed at 70°C by sandwiching the pellet between two sheets of PEO (soaked in 1M LiClO_4) and Li foils. By applying a constant voltage (25–100 mV), the DC current was recorded.

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