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Engineering Materials for Electrochemical Energy Storage via Ionic Liquid and Deep Eutectic Solvent Synthesis Media

Gaël Minart^{1,2,4,*}, Laurence Croguennec^{1,2,3}, Jacob Olchowka^{1,2,3,*}

¹ CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France

² RS2E, Réseau Français sur le Stockage Electrochimique de l'Energie, FR CNRS 3459, F-80039 Amiens Cedex 1, France

³ ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France

⁴ CIC Energigune, Parque Tecnológico de Álava, Albert Einstein 48, 01510 Miñano (Spain)

Abstract

The development of high-performance electrode and solid electrolyte materials is crucial for the advancement of next-generation electrochemical energy storage systems. Among emerging synthesis strategies, ionic liquids (ILs) and deep eutectic solvents (DESs) have gained increasing attention as alternative reaction media due to their unique physicochemical properties, including high thermal stability, wide electrochemical stability window, low vapor pressure, and tunable composition and polarity. These features offer unprecedented control over particle morphology, composition, and surface chemistry, enabling the formation of novel or metastable phases, as well as *in situ* surface functionalization or generation of homogeneous carbon coatings through post-annealing treatments. Despite these promising attributes, the implementation of ILs and DESs at an industrial scale remains to date limited. Major challenges include high viscosity, recycling difficulties, high costs, and a lack of large-scale proof-of-concepts. After introducing ILs and DESs, and their specific properties, this review critically evaluates the potential and limitations of IL- and DES-based synthesis methods in comparison to conventional techniques such as solid-state and hydrothermal approaches. The benefits and impacts of these uncommon solvents on material morphology and functional properties are discussed, along with a systematic comparison with the electrochemical performance of similar materials synthesized via classical methods. This review further discusses the prospects for industrial integration and highlights key areas where further research is essential. Finally, this article provides some perspectives that would allow for mastering these synthesis approaches and developing optimized materials for electrochemical energy storage.

Keywords

Battery materials synthesis; ionic liquids; deep eutectic solvents; nanomaterials; surface functionalization; ionothermal synthesis; surface engineering; electrochemical energy storage; particle morphology control; solid electrolyte.

E-mail: jacob.olchowka@icmcb.cnrs.fr and gminart@cicenergigune.com

1. Introduction

Batteries serve as the foundation of modern energy storage technologies, enabling a wide range of applications, from portable electronics to electric vehicles and grid-scale energy systems. The performance of a battery, including its energy density, power capability, cycle life and safety, is intrinsically linked to the properties of the electrode and electrolyte materials used. Indeed, their composition, crystallinity, particle size, morphology and surface chemistry play critical roles in determining the electrochemical behavior of the electrodes^{1,2}. Therefore, mastering materials synthesis is essential to achieve precise control over factors such as the purity and homogeneity of the material, as well as its structural and morphological properties which can significantly affect ionic and electronic conductivity, as well as the material's mechanical and thermal stability. For example, limited particle growth with the formation of nanoparticles reduces ion diffusion distances within the solid and enhances reaction kinetics for low conductive active materials such as LiFePO_4 . On the other hand, careful doping or surface modifications can improve their electronic conductivity and stability under cycling conditions³⁻⁵.

A wide range of methods exists for synthesizing inorganic battery materials, each with unique specific features that give access to various compositions, atomic structures and particle morphologies. Methods like solid-state synthesis (or the ceramic method) are widely used and easy to scale up. This approach involves mixing solid reagents—typically powders—and heating the mixture at moderate to high temperatures in air or under a controlled atmosphere (e.g., Ar, H₂, O₂) to obtain the desired (thermodynamically stable) materials. Another common approach is hydrothermal or solvothermal synthesis, which uses a liquid medium such as water to dissolve the reagents, facilitating a more homogeneous distribution of precursors than solid-state methods.

Each synthesis method for energy storage materials presents specific limitations and operational constraints. For example, solid-state reactions often present challenges in achieving atomic-scale homogeneity, even after intensive mechanical milling and multiple heat treatments, and they offer limited control over particle size distribution. These factors can result in suboptimal material performance. Similarly, solvothermal synthesis, while effective, requires pressurized vessels and subsequent solvent post-treatment, making it less practical for large-scale industrial applications due to safety and cost concerns. Moreover, each method operates within distinct temperature and pressure ranges, limiting the flexibility of synthesis conditions. Co-

precipitation methods are typically conducted at low temperatures and atmospheric pressure, hydro-solvothermal methods using common aqueous or organic solvents operate at low to medium temperatures under pressure, while solid-state methods demand high temperatures to initiate reactions between precursors (Figure 1). In this context, exploring novel and non-classical synthetic routes has become increasingly important, especially to explore the possibility of synthesizing materials in the temperature gap between the classical gentle chemistry approaches and solid-state reactions.

ILs and DESs, thanks to their unique physical properties, offer access to unconventional reaction environments, opening the possibility of discovering new materials (Figure 1)⁶. These solvents can provide a tunable reaction environment, stabilize specific reaction pathways, promote uniform particle growth, and enable the synthesis of new phases or particles morphologies that are challenging to achieve with more conventional methods⁷. By leveraging such approaches, it is possible to both synthesize new material compositions or polymorphs and/or optimize existing electrode/electrolyte materials for enhanced performance, paving the way for the next generation of high-performance batteries⁸.

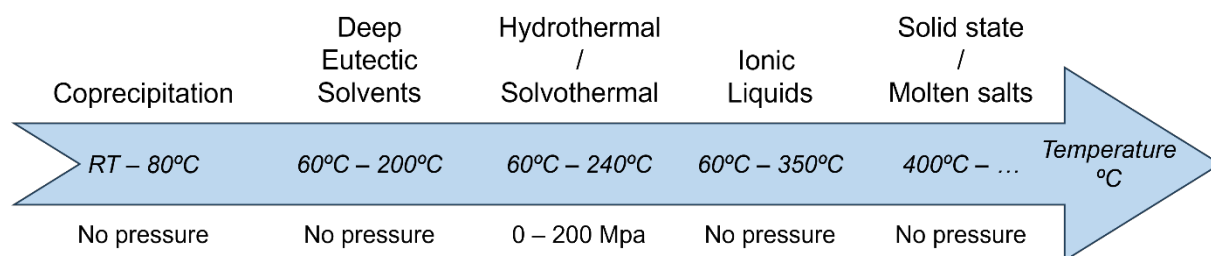


Figure 1. Representation of the most common synthesis approaches used for energy storage materials and their approximative experimental conditions (range of temperature and absence/presence of pressure).

This review aims to demonstrate the possible benefits and limitations of employing ILs and DESs as tailored media for the synthesis of energy storage materials. Rather than treating ILs and DESs separately, this manuscript highlights their complementarity through their unique properties offering multiple possibilities of tuning composition, particle size and morphology, and functionalizing particles surface⁹. It begins with an overview of the characteristics and properties of both classes of solvents. Subsequently, specific examples from the literature will be detailed and discussed to illustrate the advantages offered by ILs and DESs in various contexts. This part is divided into five thematics and intends to give an overview of the diverse

materials obtained by using these solvents as synthesis media and the underlying mechanism during their syntheses. These examples encompass the synthesis of electrode and electrolyte materials for a range of electrochemical devices, including conventional Li-ion and Na-ion batteries, supercapacitors, and all-solid-state batteries.

Beyond the scientific analysis, the manuscript concludes with a discussion and perspectives on the potential for large-scale development of these unconventional synthesis approaches.

2. Ionic Liquids versus Deep Eutectic Solvents

ILs are a class of purely ionic, salt-like materials that remain in a liquid state at unusually low temperatures, typically below 100°C, according to the commonly accepted definition^{10,11}. This low melting point primarily results from the large size and structural asymmetry of the cation and/or anion, which disrupts structure compacity and inhibits crystallization¹². The first ionic liquid, triethylammonium nitrate, was synthesized in 1914 by Paul Walden¹³. Over a century later, ILs have emerged as a hot topic in chemistry, particularly within the battery community, due to their applications as electrolytes,¹⁴ in battery recycling,¹⁵ and as reaction media for materials synthesis¹⁶. Indeed, they possess interesting features for these applications such as high thermal (Figure 2) and electrochemical stability, low vapour pressure, high ionic conductivity and non-flammability for the large majority. In the case of materials synthesis, their nearly infinite tunability in terms of composition allows to adapt their “solvent” properties such as viscosity, chemical and thermal stability depending on the need. For instance, their abilities to be either hydrophobic or hydrophilic give the possibility to synthesize highly moisture sensitive phases in a liquid medium. They can also serve as structure-directing agent, which can lead to original morphologies due to particles growth along specific atomic plans¹⁷. Finally, ionic liquids can functionalize the surface of the particles synthesized by an ionothermal method, resulting eventually in a beneficial impact on electrochemical performance⁴ or moisture sensitivity,¹⁸ these points will be discussed later.

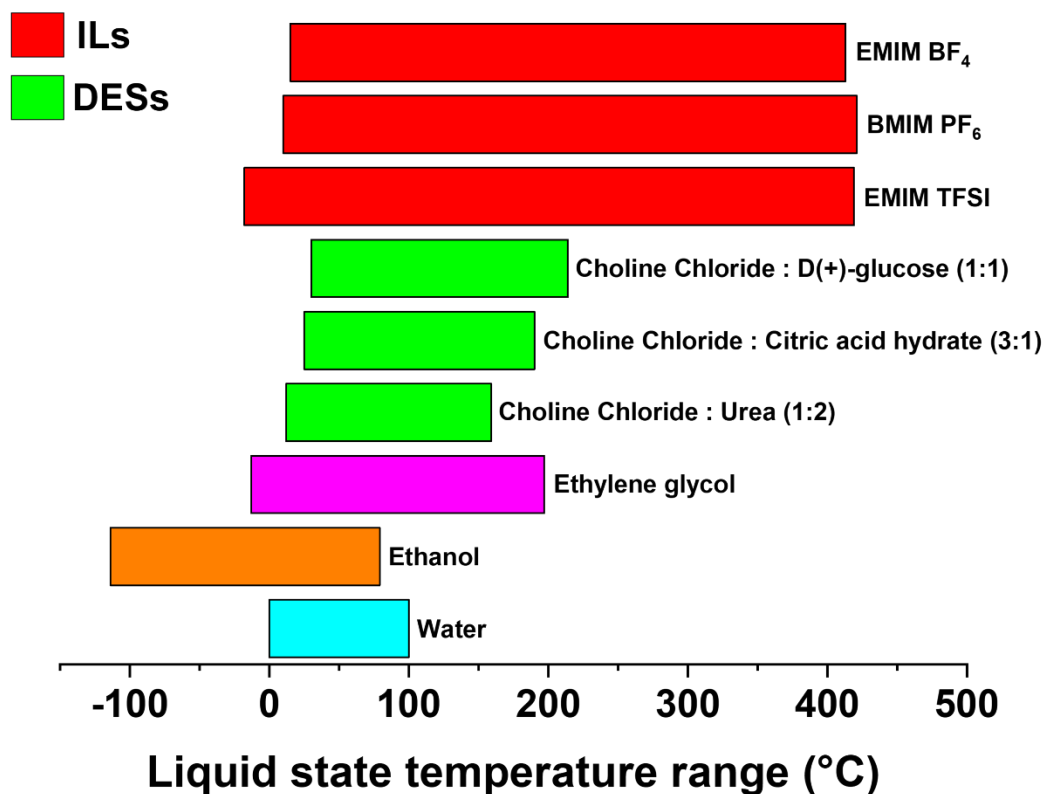


Figure 2. Comparison of the temperature stability range of the liquid phase of diverse solvents at ambient pressure.

On their side, DESs can be considered as the ionic liquids “little brother” because of the large number of similarities between them as summarized in Figure 3. DESs were discovered more than 80 years after ILs, and the first reported work on DESs was done by Abott *et al.* in 2001 who report the mixture of ZnCl₂/SnCl₂ with a quaternary ammonium salt¹⁹. DESs possess a good thermal stability but their operational temperature range is generally narrower than ILs (Figure 2). They can easily dissolve organic or inorganic compounds such as metal oxides and have low vapour pressure. Finally, both ILs and DESs are highly tunable, which can be very interesting for tailoring adapted solvents physicochemical properties for singular applications.

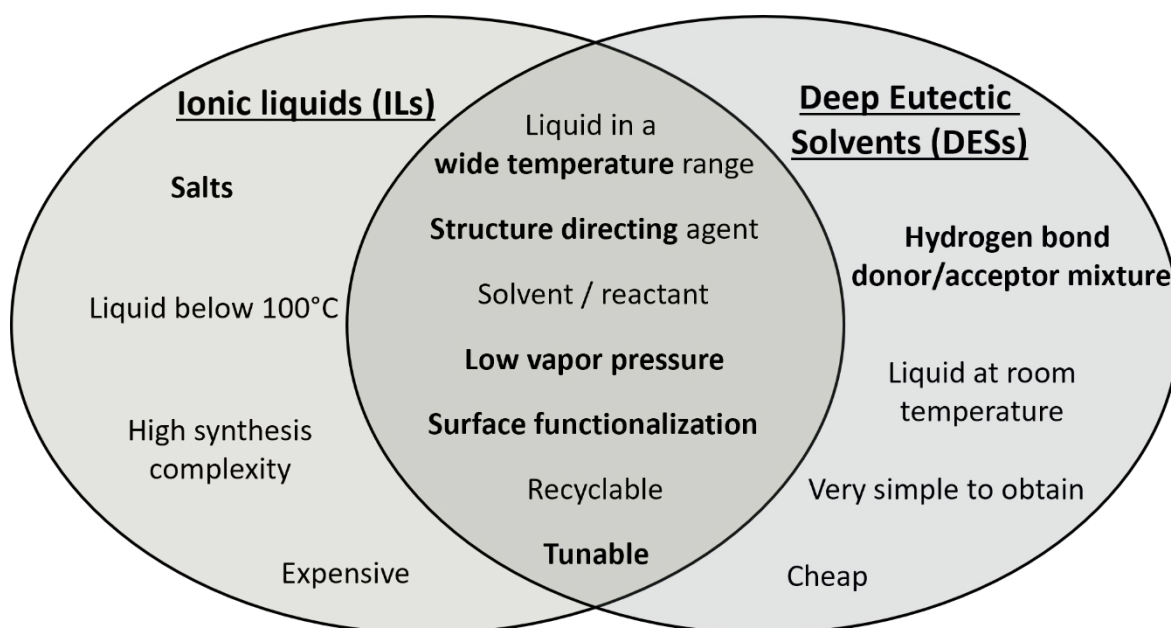


Figure 3. General characteristics and properties of ionic liquids and deep eutectic solvents.

Even though DESs and ILs are considered very similar, their nature differs in terms of composition and production. In fact, ILs are salts, thus composed of an anion and a cation, while DESs are made from the mixture of Hydrogen Bond Donors and Acceptors (HBDs and HBAs respectively) (Figure 3). Therefore, the physical interactions occurring in ILs mostly come from the ionic forces between the charged species, whereas DESs mainly consist of nano-structured hydrogen bond network solutions²⁰. Additionally, DESs are much easier to synthesize, their manufacture consists in mixing (and heating) its components, which are often commonly available. On the contrary, some ionic liquids require rather complex and heavy procedures that can be decomposed in several steps such as ion exchange, purification and distillation, explaining why these solvents are usually expensive, especially compared to DESs²¹.

There are three types of ionic liquids: zwitterionic, protic and aprotic. The first ones are composed of neutral entities because the cationic and anionic parts are covalently bonded together in contrary to other ILs, this type of solvent is more adapted for membrane applications. Protic ionic liquids (PILs), the cheapest ones, are obtained by the neutralization of a Brønsted acid with a Brønsted base, resulting in a proton transfer from one to the other. However, due to their nature, PILs possess a non-negligible vapour pressure²² and have rather low boiling temperature compared to aprotic ionic liquids (APILs). The latter, often obtained by quaternization reactions, are therefore more adapted for material synthesis, as their decomposition and vapour pressure can be negligible up to medium-high temperatures (300°C-400°C)¹⁶. Their composition is highly tunable thanks to the large number of anions and cations

possible mixtures, which will have a huge impact on their physical properties (Figures 3 and 4).

On the other side, there are four types of DESs: organic salt/metal salt-based (type I), organic salt/metal salt hydrate-based (type II), organic salt/HBD-based (type III) and finally metal salt (hydrate)/HBD-based (type IV). Type III DESs are the most adapted for inorganic materials synthesis thanks to their ability to solvate a large number of oxides and transition metal-based compounds. Regarding the other types, especially types I and II, they are usually employed for metal-based synthesis by methods such as electrodeposition or electropolishing^{23,24}. Type III DESs are composed of an organic salt, usually a quaternary ammonium salt, and a hydrogen bond donor. One of the most known example in the literature is the Choline-Chloride/Urea mixture (called Reline) in a stoichiometric ratio of 1:2²⁵. Similarly to ILs, the number of options in terms of HBDs/HBAs combination is almost infinite (Figure 4). Besides the number of different DESs is accentuated with the possibility to vary the relative ratio in composition or mix more than two reagents^{26,20}. All these parameters have an impact on the solvent physical properties such as viscosity and thermal stability.

Therefore, by playing on the composition of ILs or DESs, it is possible to tailor the desired solvent according to the needs for a specific synthesis. Taking the exemple of ILs, the cation alkyl chain(s) length will have an influence on the viscosity but also on the microphase separation (chain/ring -i.e. preventing agglomeration) resulting in faster kinetics and particle size increase when the number of carbon is increased^{27,28}. Similarly, having cations and anions with reduced size, limited symmetry and limited hydrogen bonds interactions lowers the IL viscosity but also increases its melting point^{29,30}. For instance, decreasing the alkyl chain length from butyl to ethyl for the 1-alkyl-3-methylimidazolium tetrafluoroborate decreases the viscosity from 103 to 25.2 mPa*s (at 25°C) and increases the melting point from -80°C to 15°C. The same applies for DESs, their viscosity strongly depends on the intermolecular interactions occurring in solution. Consequently, for most of the choline-chlorine based DESs, which are among the most widely used, the viscosity escalates with the salt concentration³¹.

Some specific reagents can also bring particular properties for targeted applications. For instance, ILs containing perfluorinated anions are known to be hydrophobic while ILs with anions composed of acetates, thiocyanates or dicyanamides are more hydrophilic³². Concerning DESs, the majority that are reported for material synthesis are hydrophilics and the addition of water can even be beneficial, as it will participate to the hydrogen bond network. A small water quantity can also help to reduce viscosity and facilitates the solubility of salts²⁴. However, it is

possible to obtain hydrophobic DESs by mixing quaternary ammonium salts with a carboxylic acid or alcohol that both possess very long alkyl chains ³³. Another example of quasi-hydrophobic DES that can be found in the literature is the choline chloride : sesamol (1:3). It is used mostly for liquid-liquid microextraction in organic mediums. Busato *et al.* showed for example that the mixture with methanol was completely homogeneous and thus interesting for its extraction as MeOH can be used as a dispersant ³⁴. On their side, Yao *et al* demonstrated that the synergistic effect between a DES made of choline chloride : lactic acid (1:2) and ethanol improved the digestibility of biomass for bioethanol production thanks to a higher glucose yield and lower lignin condensation ³⁵. Finally, a study conducted by Zuo *et al* ³⁶ also showed that ethanol or water addition in different concentrations in DESs had some effect on the molar volume and viscosity, with first a decrease of the latter and then an increase up to certain concentration, emphasizing their tunability by a simple addition of solvent.

Thanks to all the tailoring possibilities of these so called “neoteric” solvents for inorganic materials synthesis, ILs and DESs have attracted a lot of attention for the synthesis of inorganic electrode and electrolyte materials for various electrochemical energy storage systems. The next part of this manuscript will give some insights into the reported works about this topic, with an attempt to highlight the numerous advantages of this synthesis approach such as morphology and composition control or coating application.

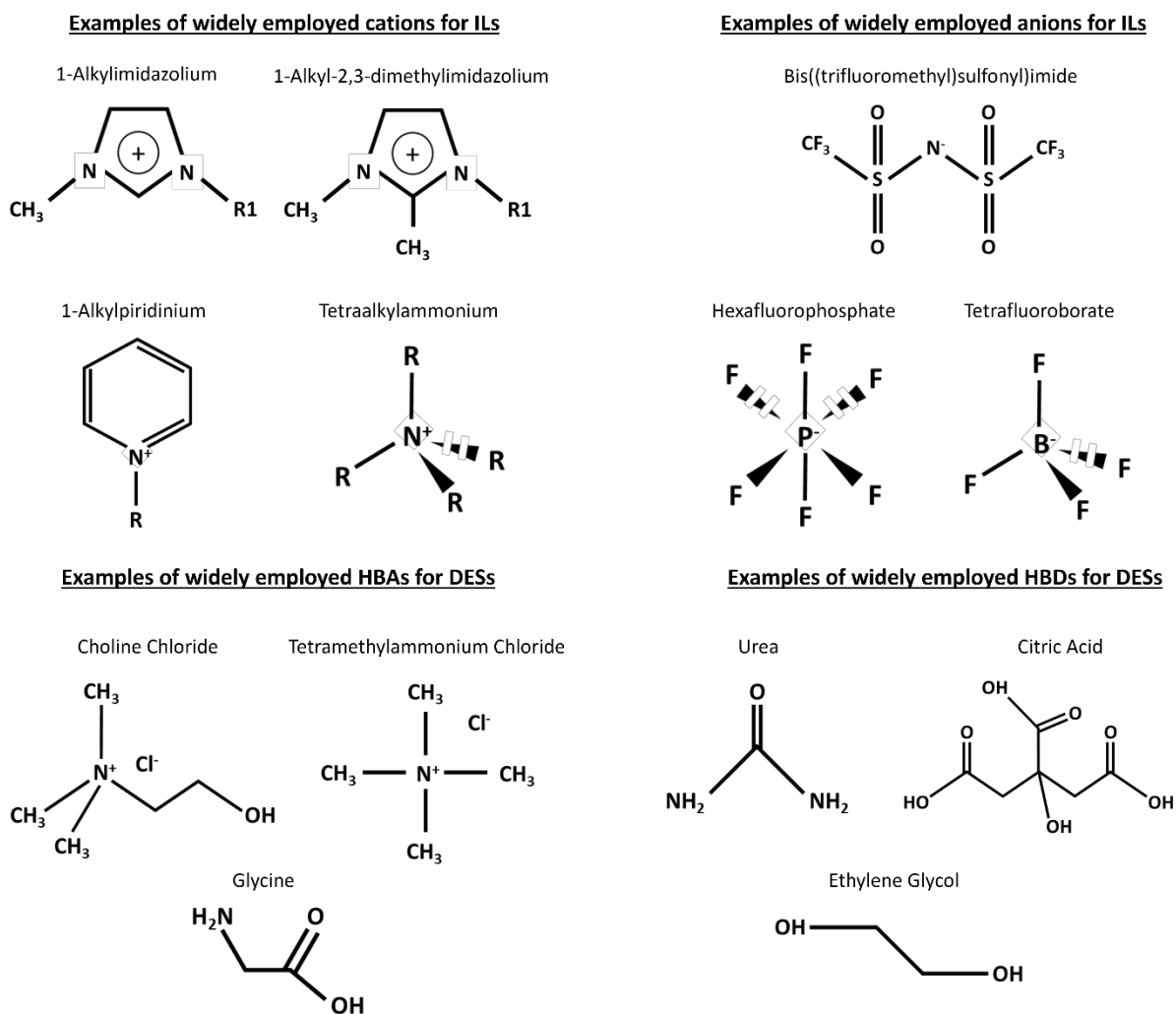


Figure 4. Examples of the different possible cations and anions for the elaboration of ionic liquids as well as the different HBDs and HBAs commonly used for deep eutectic solvent compositions.

3. State of the art on materials synthesis for energy storage applications

3.1 Particles morphology control via direct synthesis in ILs / DESs

Controlling the particles morphology through soft chemistry approach with classical solvents is already well established and even commonly employed at industrial scale. Indeed, by playing on the reagents concentration, synthesis temperature and time, or by adding additives, it is possible to obtain a wide range of different particle sizes and shapes^{37,38}. In the case of ILs and DESs, their nearly infinite possible compositions also give rise to a wide playground to engineer a material morphology without any additives.

In the field of battery materials, a huge amount of work has been initiated by Recham *et al.*¹⁷ and Barpanda *et al.*²⁸ who synthesized LiFePO₄ (LFP) and LiMnPO₄ (LMP) in various imidazolium-based ILs and investigated the impact of alkyl chain length and the nature of its terminal group on the particles shape and size (Figure 5). First, both studies highlighted the fact that using ionic liquids containing –OH terminal groups greatly improve the reagents solubility and allows a decrease of the synthesis temperature of the polyanionic materials. Interestingly, it was also observed that for LFP, the use of –CN based ILs initially promoted nanoparticle growth along the $\langle 10\bar{1} \rangle$ direction until a critical needle length is reached, and then, a single crystal growth along the direction $\langle 010 \rangle$ is induced by needles edge-merging mechanism due to surface energy minimisation phenomenon. On the contrary, LMP particles tend to adopt a large biprism-shaped form when synthesized in the same ionic liquid, which reveals that the impact of IL nature depends on the targeted material chemistry.

Additionally, it was demonstrated that an increase of alkyl chain length develops the microphase separation, which will induce faster kinetics and results in larger particles size, unlike branched ILs leading to smaller particles. This phenomenon was also supported by the work of Sideris *et al.*³⁹, where LFP crystallinity increased when being synthesized in solvents with longer alkyl chains. Besides, Recham *et al.* also pointed out that very long carbon chain on imidazolium ring induces different growth mechanisms, which allow to change the orientation growth and tailor particles morphology¹⁷. Finally, these pionner works reported by Tarascon's group highlighted as well the excellent energy storage performance of LiFePO₄ obtained in ionic liquid media although no carbon coating was applied on these phosphate based electrode materials¹⁷.

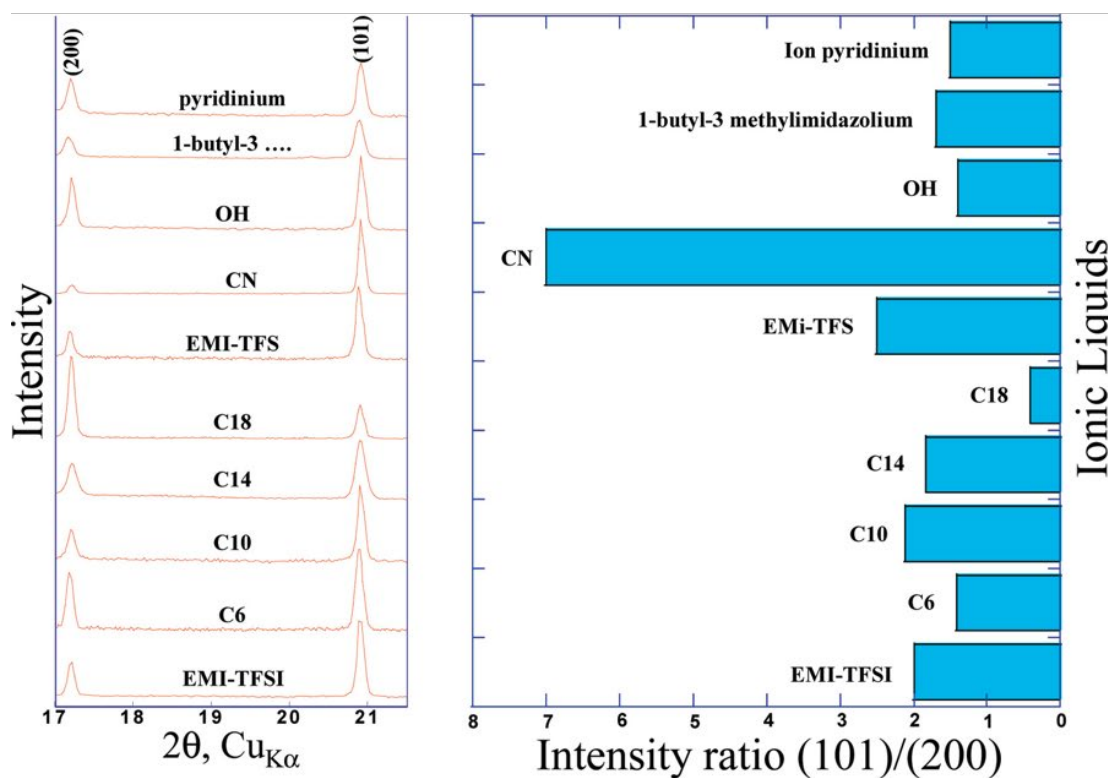
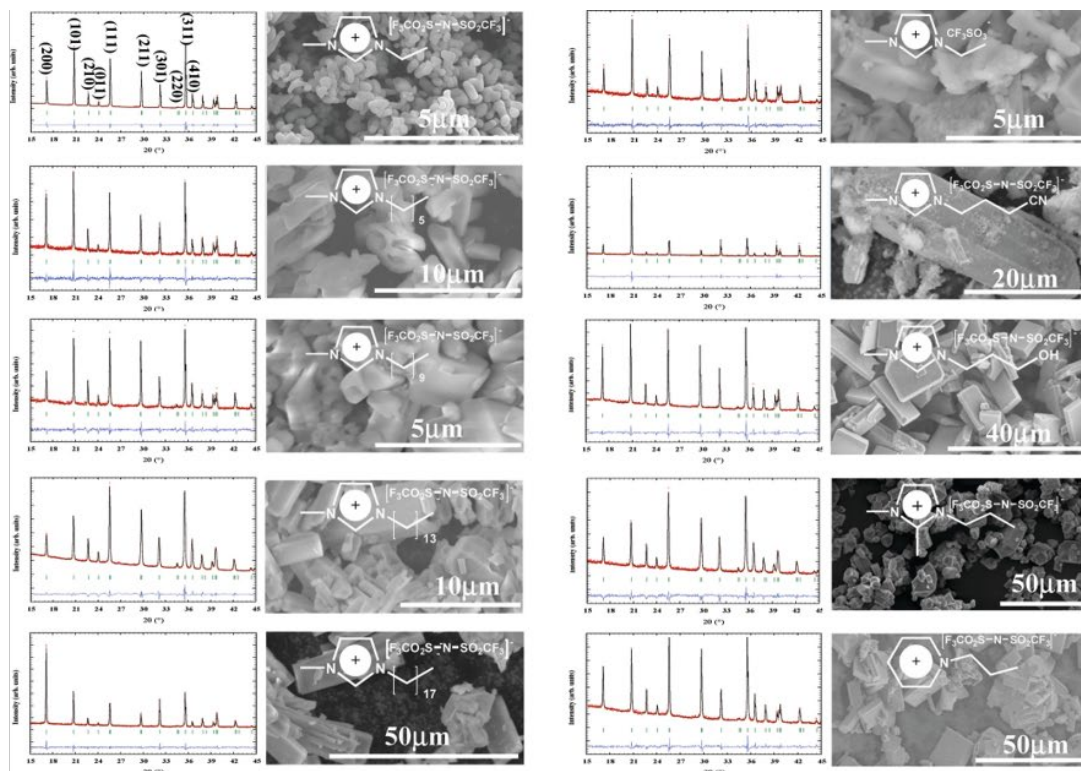


Figure 5. Illustration of the influence of the ionic liquid composition on LFP morphology and preferential orientation observed on XRD pattern and effect of the nature of the ionic liquid on the (101)/(200) XRD intensity ratio. Reproduced from [17]. Copyright 2025 American Chemical Society.

In another study, LFP nanoparticles could also be obtained by electrochemical assistance in an EMIM TFSI bath containing FeCl_3 and Li_3PO_4 ⁴⁰, thanks to the wide electrochemical and thermal IL stability window, as LFP precipitation is only possible at temperatures above 120°C ⁴⁰. This uncommon synthesis method gave even the possibility to crystallize the material directly on a Li_3PO_4 substrate and highlights the possibility of using ILs as synthesis medium in less conventional synthesis approaches.

In addition of conducting classical syntheses that involve dissolution of the precursors, nucleation and particles growth, ILs and DESs are well adapted media to conduct topotactic reactions, allowing to control particle morphology of the resulting material through the control of precursor particle morphology. The work of Olchowka *et al.*⁴¹ represents a perfect example of such synthesis strategy. In their study, a custom made $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was mixed with NaF in EMIM TFSI to synthesize $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$ (NVPFO₂) via a topochemical reaction, involving the ionic exchange of water molecules with sodium and fluorine, accompanied by a reduction of vanadium to maintain charge balance. As a result, the specific 2D platelet morphology of the precursor was preserved for the active material (Figure 6). Interestingly, the resulting NVPFO₂-IL electrode material exhibited a solid solution driven mechanism upon cycling rather than a phase transition usually observed for this composition. The authors suggested that the sodium diffusion path along the $\langle 110 \rangle$ direction, oriented parallel to the platelet surface, could result in such phenomenon. The same team also employed a similar platelet-morphology layered precursor, this time incorporating a partial Mn for V substitution, to further conduct an analogous topochemical reaction and obtain a partially cationic substituted $\text{Na}_{2.85}\text{V}_{1.6}\text{Mn}_{0.4}(\text{PO}_4)_2\text{F}_{2.4}\text{O}_{0.6}$ electrode material⁴². Quite interestingly, they found that the resulting material possesses an uncommon under-stoichiometry in Na, which was confirmed by chemical titration, Rietveld refinement and electrochemistry. Finally, they also reported that several synthesis trials in more classical solvents led to the precursor decomposition leading to the obtention of mixture of different phases such as $\text{Mn}_2\text{PO}_4\text{F}$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$, underscoring the unique properties of ILs to access to both such peculiar particles morphology and unique chemical composition.

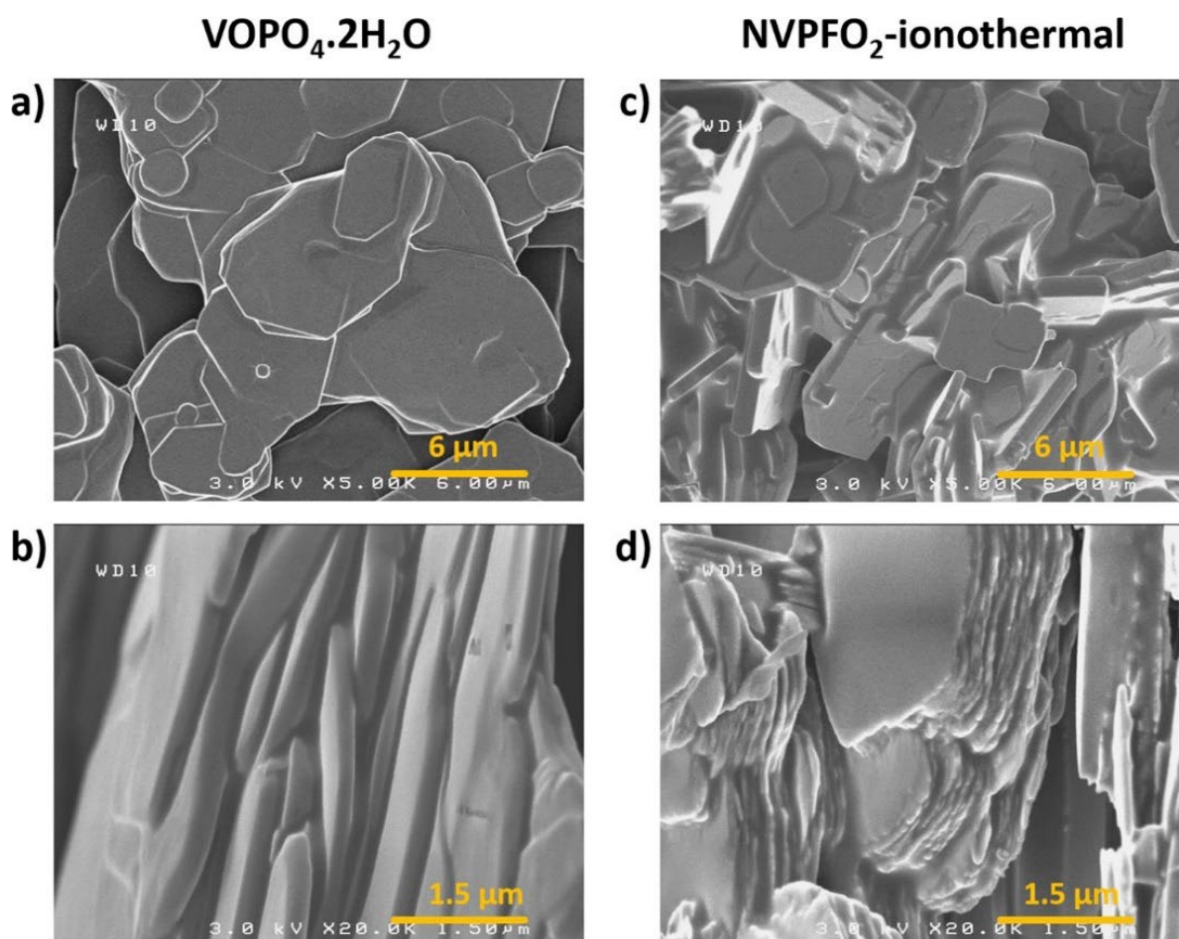


Figure 6. SEM images of the 2D platelets-shaped particles of a), b) the $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ precursor and c), d) the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$ active material. Reproduced from [41]. Copyright 2025 American Chemical Society.

Dealing with topochemical approaches, Li *et al.*⁴³ reported the possibility to obtain a HTB-type $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ phase as electrode material for lithium and sodium batteries via a top-down synthesis from $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. However, this time the microsized precursor was broken down into nanostructured particles during the dehydration process. This transformation enabled a higher yield (100% versus 25%) and improved phase selectivity and purity compared to traditional bottom-up approaches. Besides, the authors highlighted the simplicity and high reproducibility of the process, as well as the possibility to scale it up and recycle the ILs, making it very attractive.

To conclude this first section, ILs and DESs offer outstanding morphology tunability, primarily arising from their wide diversity of chemical architectures, which directly influence synthesis thermodynamics and particle surface energies. Unlike conventional solvents that often require additives such as chelating agents or surfactants, tailoring the composition of ILs or DESs alone

is sufficient to induce pronounced changes in particle morphology during direct synthesis. Moreover, their ability to stabilize certain solid phases in a liquid medium - phases that would otherwise dissolve under conventional conditions - enables their use in topochemical reactions, thereby preserving precursor morphology that can be deliberately engineered prior to synthesis.

3.2 *ILs / DESs synthesis media for nanomaterials*

In addition to enabling the engineering of particle shape and promoting preferential orientation growth, these solvents facilitate the synthesis of uniform nano-sized materials. This was illustrated by the work of Xiong *et al.*⁴⁴ and Wu *et al.*⁴⁵ with the synthesis of Fe₂O₃ nanospindles (≈ 100 nm) and LiMnPO₄ nanorods (100–150 nm length), respectively, in choline chloride based deep eutectic mixtures. Thanks to their small particle sizes obtained due to the surfactant properties and high viscosities of the DESs, both nanomaterials exhibited excellent rate capabilities and capacity retention (e.g. 106 mAh.g⁻¹ at 5C and 93% capacity retention after 100 cycles at 1C for LiMnPO₄). The electrochemical performance was particularly enhanced for the LiMnPO₄ particles synthesized in an ethylene glycol/choline chloride DES compared to solely in ethylene glycol, although an in-depth comparison of the microstructure is missing to understand precisely the impact of DESs solvent. In another study, Zhao *et al.*⁴⁶ compared different synthesis methods for Co₃V₂O₈ and found out that ionothermal synthesis in 1-butyl-3-methylimidazole bromide resulted in uniform spherical nanoparticles exhibiting a higher capacity with a better retention compared to the irregular large-block that were obtained through the traditional hydrothermal method.

Similarly, a performance study was conducted on Li₃V₂(PO₄)₃/C composites (LVP) obtained from precursors that were synthesized in three different ILs to evaluate their impact on the particles microstructure and energy storage performance⁴⁷. The synthesis process involved dissolving sucrose, LiOH, V₂O₅ and H₃PO₄ in EMIM BF₄, EMIM OAc or EMIM OTf, along with the addition of hydrazine hydrate. The mixture was then heated at 200°C for 10h, followed by sintering the retrieved powder at 700°C under argon-hydrogen (5% H₂) for 2h. In this study, the ILs were used as structure-directing agents due to their ability to adsorb onto the surface of the powder, resulting in a uniform precursor particle morphology that was preserved during the calcination process. Comparing the impact of the different ILs, the LVP particles obtained with EMIM OAc exhibited a uniform submicronic size, the smallest in the series, which was attributed to the smaller surface tension of this IL among the three, and leading to the highest specific capacity, rate capabilities and capacity retention when tested as positive

electrode material for Li-ion batteries. This superior performance can be attributed to the reduced and homogeneous particle size, as well as the smaller charge transfer resistance and enhanced diffusion coefficient revealed by electrochemical impedance spectroscopy, underscoring the practical influence of ionic liquid composition used during the synthesis on resulting electrode material electrochemical performance.

Concurrently, several studies employing ILs/DESs for the synthesis of eco-friendly electrode materials gave very promising outcome. For instance, Rangaswamy *et al.* synthesized LiTiPO₄F/C using 1,2-dimethyl-3-(3-hydroxypropyl) imidazolium dicyanamide⁴⁸. The electrode material exhibited encouraging energy storage performance thanks to its limited particles size (down to 100 nm) and good crystallinity. Specifically, a respectable specific capacity of 150 mAh/g was achieved at approximately 2.0 V vs. Li⁺/Li and a rate of C/15, with a capacity retention of 85 % after 200 cycles. Similarly, Shiprath *et al.*⁴⁹ worked on a low temperature process, using a choline chloride/ethylene glycol DES, to obtain sedorenkite Na₃MnPO₄CO₃ (NMPC) electrode material for aqueous Na-ion batteries. The resulting nanoparticles have a median size between 20 and 25 nm with a spherical shape. Electrochemical tests showed that NMPC undergoes a reversible sodium insertion/extraction mechanism in an aqueous electrolyte versus a NaTi₂(PO₄)₃ negative electrode. However, although the extracted capacity of 77 mAh/g remained stable for 100 cycles, it only represents 40 % of the theoretical capacity, giving space for further optimization.

More recently, Tao *et al.* employed ionothermal synthesis to nanostructure carbon/TiO₂ composites for supercapacitor applications⁵⁰. Utilizing the solvent and surfactant properties of various imidazolium bis(trifluoromethylsulfonyl)imide-based ionic liquids, nano TiO₂ embedded in an IL matrix was obtained at low temperature before undergoing carbonization at 600°C in N₂ atmosphere. The resulting [CNPIIm][NTf₂]-based C/TiO₂ porous composite featured a C content of 59.4 wt%, a TiO₂ grain size around 7 nm and a high specific surface area of 412.6 m²/g. In this experiment, the IL acted both as a solvent and a carbon precursor, and its pyrolysis facilitated the partial reduction of Ti⁴⁺ to Ti³⁺ in the anatase phase (leading to defectitive TiO_{2-δ}), enhancing the intrinsic electrical conductivity of the electrode material. Ultimately, this composite delivered capacitance values higher than 70 F.g⁻¹ at 500 mV/s in 1M KOH (≈ 20 mAh.g⁻¹ at 1800C (a full charge in 2 s)), underscoring the advantages of ionic liquids in synthesizing nanostructured electrode materials with excellent high-rate performance and long-term cycling stability.

To conclude this second section, which follows directly from the discussion on morphology control, various examples from the literature demonstrate that ILs and DESs are also well-suited for the synthesis of nanosized materials. Indeed, the intrinsic surfactant-like properties of these solvents promote the multiplication of distinct nucleation sites within the reaction medium, ultimately leading to the formation of nanoscale particles. However, it is important to emphasize that these outcomes are not systematic and strongly depend on synthesis parameters such as alkyl chain length, reaction time and temperature, precursor concentration, and the nature of the starting materials.

3.3 *ILs and DESs as co-solvents or additives*

To further design the particles shape, IL or DES can be mixed with other solvent(s) in different ratios, such as water, to change the synthesis medium characteristics. For example, Datta *et al.*⁵¹ showed that it was possible to obtain diverse V₂O₅ particle morphologies, ranging from 3D microbeads to 1D nano-units, by simply adjusting the DES/water ratio, which leads to distinct particles formation mechanisms. Among the series of different V₂O₅ particles morphologies, the best energy storage performance was achieved for the 2D nanosheets, with a capacity retention of 64% after 100 cycles at 250 mA/g. Similarly, in the work of Li *et al.*⁵², the particle morphology of a Ni_{0.5}Mn_{1.5}(OH)₄ precursor was tailored according to solvent mixture ratio, from [C12mim]Br ionic liquid diluted in water to pure ionic liquid solution. In high concentration in aqueous solution, ILs based on 1-alkyl-3-methylimidazolium cations exhibit aggregation behavior and form micelles in solution, inducing particles aggregation. Consequently, the morphology of the positive electrode material shifted from flake-like and irregular particles for the most diluted solution to agglomerated flake-like structure for the most concentrated solution in ionic liquid. Furthermore, the precursor morphology was maintained in a certain degree after the calcination step with a lithium precursor to form the spinel LiNi_{0.5}Mn_{1.5}O₄. In the end, the higher the ionic liquid concentration used for precursor synthesis, the better the energy storage performance of the electrode material. The strategy to tailor the precursor by its synthesis in a ionic liquid based-medium followed by a solid state synthesis was also explored by He *et al.*⁵³ with the preparation of MnF₂ hollow spheres (HS) that served to obtained both LiMn₂O₄ and Mn₂O₃ with preserved HS shape.

In addition of being employed as co-solvent, ILs can also be incorporated in a low quantity to be used as classical surfactant⁵⁴. In this perspective, Invernizzi *et al.* investigated the impact of a series of imidazolium bromide based ILs, used as surfactant/template during the

coprecipitation synthesis of cobalt oxyhydroxide (H_xCoO_2)⁵⁵. They found that the incorporation of ILs allowed to obtain particles of 5 nm and a H_xCoO_2 -IL with specific surface area and mesoporosity of 256 m²/g and 0.43 cm³/g versus 160 m²/g and 0.16 cm³/g for the material obtained without ionic liquid. Their results revealed that the length of the alkyl chain (ethyl, hexyl, or decyl) on the 1-alkyl-3-methylimidazolium cation had a limited impact on the specific surface area but influences the energy storage performance of the electrode materials. Indeed, the increase of alkyl chain length resulted in a capacity raise, going from 40 to 50 mAh/g at 0.2C in 5M KOH from ethyl to decyl carbon chain length. Besides, without ionic liquids the cobalt oxyhydroxide delivered 34 mAh/g in the same cycling conditions highlighting the benefits of incorporating ionic liquids in the synthesis medium. In another study, Bharate *et al.* demonstrated that using an ionic liquid as capping agent changed the particle morphology of the synthesized α -MnO₂ from spheres to nanorods, which was beneficial to increase material performance when tested as active material for supercapacitor applications⁵⁶.

The influence of ionic liquid additive was also tested for the hydrothermal synthesis of a precursor for Li-rich layered oxide (H-LMNO) whose composition is associated to the solid solution between the two end-members according to the stoichiometry $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Mn_{0.5}O_2$ in the work of Xiang *et al.*⁵⁷. They showed that the addition of N-hexyl pyridinium tetrafluoroborate ionic liquid (HPy BF₄) lowered the particles agglomeration, leading to higher rate capability and cyclability compared to the same material synthesised in a classical hydrothermal process. Thanks to the ILs surfactant properties, particles agglomeration is prevented and porous secondary aggregates made of nanoparticles will be favoured, thus enhancing the diffusion of electrons and cations. In the end, the ionothermal H-LMNO (after thermal treatment with Li₂CO₃ at 700°C under air) exhibits a 9% higher capacity retention (94.3% vs 85.2% after 65 cycles), with in addition a higher initial capacity delivered on the first cycle (254.1 mAh/g vs. 242.9 mAh/g). Furthermore, this phase possesses a three times less important charge transfer resistance, proving the interest to consider employing ionothermal synthesis for these electrode materials.

Impressive results were also obtained in the case of Zhang *et al.*⁵⁸ with the development of a nano-sized Li₃V₂(PO₄)₃/carbon composite obtained through a simple synthesis in which a protic ionic liquid (PIL) was acting simultaneously as soft template and carbon source. The synthesis consisted of two steps: First, pyrrolidinium bis(trifluoromethanesulfonyl)imide (PIL) was introduced in an aqueous solution containing vanadium oxide, lithium carbonate, ammonium dihydrogen phosphate and oxalic acid, to act as template during the subsequent stirring at 80°C.

The resulting product (amorphous LVP/PIL) was finally pre-sintered at 350°C and then at 800°C under nitrogen to obtain crystallized LVP nanoparticles embedded in the carbon matrix issued from PIL carbonization. The resulting electrode material exhibited an interesting capacity retention and rate capabilities with almost 100 mAh/g at 100C and a remaining capacity of 75 mAh/g after 10 000 cycles at 50C (with active mass loading between 1.5 and 2 mg.cm⁻²) (Figure 7). The nanosized particles, due to the IL structure directing agent properties, coupled with the carbon matrix resulting from its calcination, show the interest in using protic ILs for such applications, especially with the advantage of being cheaper than aprotic ILs.

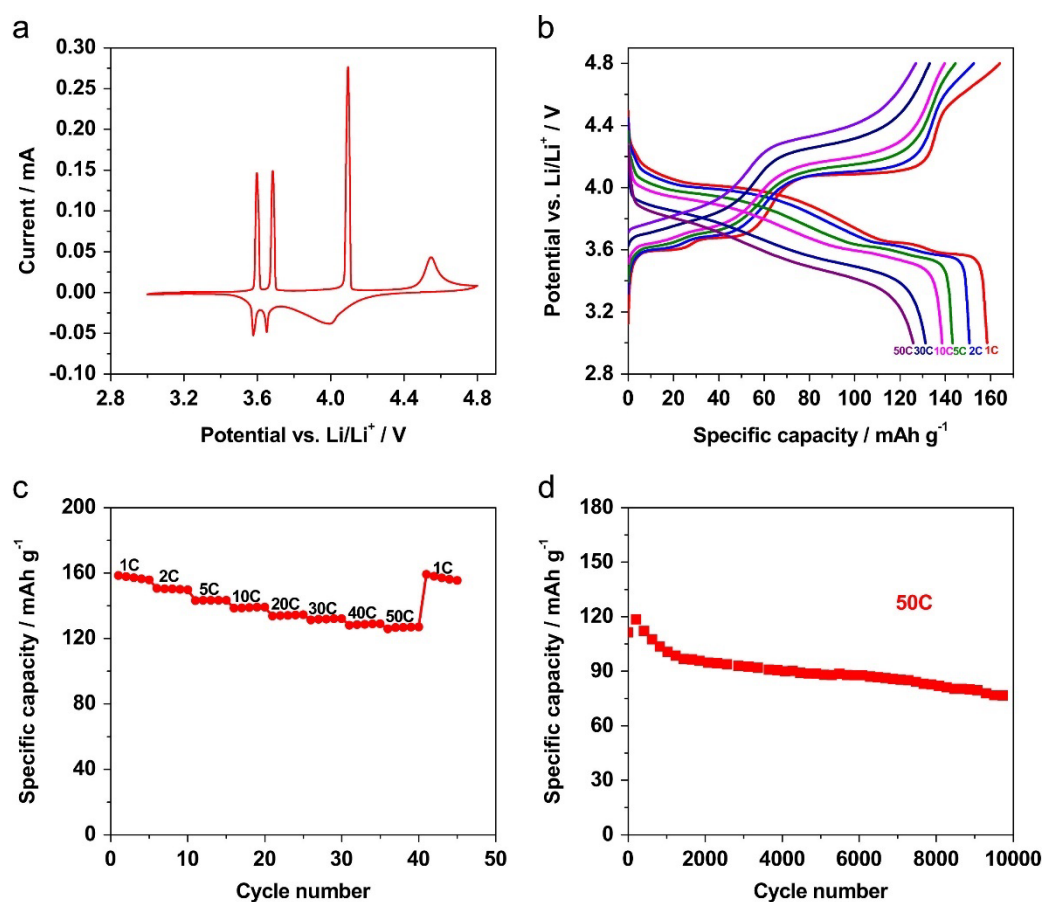


Figure 7. Associated electrochemical curves to the nano-sized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ composite. a) Cyclic voltammetry of LVP/PIL electrodes vs. Li/Li^+ at 0.05 mV s^{-1} . (b)–(d) Performance of LVP/PIL electrodes during constant current cycling. (b) Typical galvanostatic charge-discharge curve profiles and (c) specific discharge capacity of LVP/PIL electrodes when charged/discharged at various discharge current densities in the range of 1 to 50C. (d) Specific capacity of LVP/PIL electrodes during long-term cycling at 50C. Reproduced with permission from [58]. Copyright 2025 Elsevier.

Finally, ILs and DESs can also be used as co-solvents owing to their miscibility with conventional solvents, or in small amounts as additives to control particle growth. In the latter case, the use of highly diluted ILs as dispersing agents can be attractive because of the limited solvent consumption; however, this approach may raise challenges related to post-synthesis recovery and recycling. Overall, the wide range of possible solvent combinations and compositions offered by ILs and DESs constitutes a vast playground for the development of new materials with potentially unexpected or enhanced performance.

3.4 *Safe, stable and flexible synthesis media*

In addition to microstructure control, these type of solvents and more particularly ionic liquids have the advantage of being adapted for the synthesis of a wide range of compounds, even including some that are extremely challenging to synthesize in solvothermal conditions. For example, some sulphate-based and/or Fe^{2+} -based materials are known to be very sensitive to moisture, making them rather unsuitable for hydrothermal conditions⁵⁹. Besides, dealing with sulfate-based positive electrode materials, their low thermal stability limits the use of prolonged solid-state processes⁶⁰. This is why ILs are well adapted for their preparation. Indeed, some ILs allow to work in anhydrous conditions, while permitting lower reaction temperature compared to solid-state approach.

Recham *et al.*⁶¹ have demonstrated that it was possible to obtain tavorite LiFeSO_4F by topotactic reaction by mixing LiF and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in EMIM TFSI (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), leading to a similar mechanism to the work reported later by Olchowka *et al.*⁴¹ and dealing with the ionothermal synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$, but in this former case with the conservation of a rather identical atomic structure compared to that of the precursor.

Following this study on LiFeSO_4F , several partially iron-substituted tavorite phases were synthesized from $\text{Fe}_{1-x}\text{M}_x \cdot \text{H}_2\text{O}$ precursors ($\text{M} = \text{Mn}, \text{Co}$ and Ni) using the same synthetic approach and subsequently tested as electrode materials⁶². It appears possible to obtain the full solid solution from $x = 0.5$ to $x = 1$ for Ni and Co , while it was not possible to substitute Fe by Mn beyond 10 at%. This lies in the fact that LiMnSO_4F is not isostructural to tavorite LiFeSO_4F on the contrary to LiCoSO_4F and LiNiSO_4F ⁶³. This tavorite LiFeSO_4F material exhibits very promising features such as an energy density very close to that of LiFePO_4 along with better ionic and electronic conductivities. However, its moisture sensitivity is a major problem as it was shown by Zhang *et al.*⁶⁴ who demonstrated that relative humidity can have a great impact

on the powder stability, even if ionic liquid grafting can help to overcome this issue, as it will be discussed later.

The ionothermal synthesis route of the alluaudite $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$ was also explored by Dwibedi *et al.*⁶⁵. Indeed, as a Fe^{2+} and sulphate-based compound it is also moisture sensitive and with a thermal stability limited up to 450 °C, making thus ionothermal synthesis an interesting option, especially using a hydrophobic ionic liquid. Several solvents were tested such as an ethane-1,2-diol/EMI TFSI mixture, giving diverse particle morphologies such as micrometric platelets or uniform elliptical particles. The alluaudite obtained in pure ionic liquid exhibited high-voltage (ca. 3.7 V vs Na^+/Na) redox activity and delivers a reversible capacity of ~80 mAh/g at C/20, better than the alluaudite obtained from a solvent mixture (i.e. 60 mAh/g for ionic liquid-water media and 50 mAh/g for ionic liquid-diol media). The authors attributed this optimized performance to smaller particle size.

Among the families of compounds that might be moisture sensitive and thus present synthesis complexity, the fluorides have attracted a lot of attention in the last years. Indeed, their low molar mass combined with the high electronegativity of fluorine grant them with high theoretical energy densities, up to almost 500 Wh/kg for NaFeF_3 ⁶⁶. However, the process to obtain these materials can be challenging for the aforementioned reasons and even dangerous because of the use of highly hazardous chemicals such as hydrofluoric acid. This is why ILs can be interesting and more particularly fluorine-based ones. Indeed, they can serve both as solvent and reactant by acting as the fluorine source. Some works have been reported in the literature with tetrafluoroborates or hexafluorophosphates-based ILs to develop safer synthesis routes for fluoride (nano)materials^{67,68}.

Li *et al.*⁶⁹ managed to obtain two distinct nanostructured hydrated iron fluoride phases by heating iron (III) nitrate nonahydrate in BMIM BF_4 (1-Butyl-3-methylimidazolium tetrafluoroborate) acting as both solvent and reactant (fluorine source). The first material $\text{Fe}_{1.9}\text{F}_{4.75}\cdot 0.95\text{H}_2\text{O}$ was synthesized by heating the mixture at 50°C for 6h and exhibits specific capacity of 90 mAh/g for the first 10 cycles. In comparison, the $\text{FeF}_3\cdot 0.33\text{H}_2\text{O}$ material obtained through the same synthesis steps with an additional vacuum treatment for 2h is more promising. Indeed, the water removal seems to have beneficial effects on the electrochemical performance leading to an increased and stable specific capacity up to almost 160 mAh/g as well as a good rate capability. The sponge-like morphology of the particles (versus rectangular morphology for $\text{Fe}_{1.9}\text{F}_{4.75}\cdot 0.95\text{H}_2\text{O}$) has a huge impact on this improvement; a vacuum treatment reduces

the crystallite size and the particles size, leading to shorter diffusion length for lithium ions within the material. Interestingly, a prolonged vacuum step leads to a phase amorphization.

More recently, Yan *et al.* employed fluorinated ionic liquid as structure directing agent to design the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) particles morphology and as reactant to compensate F^- loss during the subsequent carbonization process of the NVPF@rGO.⁷⁰ ILs are also interesting for the dispersion of graphene thanks to interactions between the imidazolium cation and the graphene π -electrons⁷¹. Thus, ILs are particularly adapted for the synthesis of iron fluorides/graphene composites for Li-ion and Na-ion batteries as reported in the works of Li *et al.*⁷² and Jiang *et al.*⁷³. In both cases, the composites show a significant improvement in terms of rate capabilities and capacity retention, with a specific capacity up to more than 90 mAh/g at 20C for the graphene/ $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ material (ratio estimated at 17:83) at 2.5 V vs Li^+/Li ⁷². Hence, the strategy of synthesizing homogeneous active material/graphene composites in ILs is very promising to obtain efficient electrode materials thanks to the enhanced electronic conductivity of the graphene matrix but also its ability to serve as a physical support to restrain the detachment and agglomeration of the nanoparticles.

This aptitude was also applied for lithium sulphur batteries by Zhang *et al.*⁷⁴, where a microporous carbon support made from an ionothermal synthesis in BMIM H_2PO_4 , combined with an activation process, served as a host for lithium-sulphur active material. It was made to avoid the polysulfides solubilisation and to maintain the electrode integrity despite the sulphur large volume expansion upon cycling. Additionally, the graphene matrix is an effective way to enhance the electronic conductivity of the electrode. The synthesis procedure consisted in mixing D-glucose with graphene oxide in an aqueous suspension with the addition of ionic liquids. The resulting mixture was dried for 24 h in an oven at 95 °C to remove the water and subsequently heated up to 180 °C for 20h. Then, the resulting powder was sintered at 800°C under argon for 2h after being activated in a KOH aqueous solution. The electrode material was finally obtained by simply grinding the resulting micro/mesoporous graphene with sulphur and heating the mixture at 155°C for 15h in a sealed stainless-steel container. The resulting composite material exhibits very promising electrochemical performance in terms of rate capability and capacity retention, with a specific capacity up to 700 mAh/g at 2C and 600 mAh/g after 150 cycles at 1C. To make an appropriate comparison, another porous graphene material was synthesized with the same process but without involving ionic liquid: only deionised water (labelled H-GPC) was used. The results are irrefutable, the carbon matrix obtained with the BMIM H_2PO_4 (I-GPC) is by far the best performing, with almost double

exhibited specific capacity compared to the water-based processed material. This was attributed to the higher specific surface area for the I-GPC, giving a better electrolyte contact and infiltration but also to its broad pore size distribution in the micropore range (0.5 nm, 0.6 nm, 0.8 nm, and 1.2 nm) that effectively prevents the solubility of the polysulfides and ensures a fast Li^+ migration during the lithiation/delithiation processes. In comparison, the H-GPC possesses a lower specific surface area and larger micropores/mesopores, which are less effective at immobilizing sulfur and thus allow polysulfides dissolution.

Finally, Rangaswamy *et al.*⁷⁵ worked on a LiVPO_4F /graphene composite that exhibited promising performance. They synthesized themselves the 1,2dimethyl-3-(3-hydroxypropyl)imidazolium dicyanamide ionic liquid that served as a solvent for the ionothermal synthesis of the active material LiVPO_4F . In this example, the graphene was mixed with LiVPO_4F just before the electrode preparation, and not during the synthesis of the active material. What is interesting here is that the ionic liquid was specifically made for the synthesis of LiVPO_4F , because the ILs available on the market had not the characteristics required to prepare this material with success. First, the C_2 carbon on the imidazolium ring is protected by an alkyl group to prevent any reaction with basic species such as PO_4^{3-} or F^- during the synthesis and thus the IL from degradation. Recham *et al.*⁷⁶ adopted the same strategy for the ionothermal synthesis of $\text{Na}_2\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4\text{F}$ phases. Secondly, the $-\text{OH}$ radical group enables the reduction of synthesis temperature thanks to higher precursors solubility. The resulting material exhibits an honourable reversible capacity of 153 mAh/g during the first cycle for the LiVPO_4F /functionalized-graphene composite and maintains a relatively stable capacity over 250 cycles.

In another context, that of the regeneration of aged active materials for batteries, Hawley *et al.* reported a preliminary study in which they synthesized NMC811 from delithiated NMC111 using a room-temperature eutectic solution composed of $\text{LiOH}\cdot\text{H}_2\text{O}$ and nickel nitrate hexahydrate. This upcycling scalable approach, to relithiate and change the transition metal composition at low-temperature annealing shows great promises as it generates high purity and homogeneous material and is mentioned as cheaper and faster compared to classical recycling and reuse of the upscaled precursors for a new high-temperature synthesis. Nevertheless, the electrochemical performance of the material as obtained is poorer than commercially-available NMC811, highlighting the need for further development⁷⁷.

To summarize, ionic liquids are highly promising synthesis media for producing highly graphitized and porous carbonaceous materials, which can serve as supports or matrices for a

wide range of active materials. Their effective dispersion power, facilitated by π - π interactions between the imidazole rings and the carbon atoms in the graphitic layers, makes them more efficient than traditional solvents like water. These composites can significantly enhance electrode materials that suffer from sluggish kinetics, large volume expansion, or dissolution into electrolyte during cycling. More generally, ILs and DESs are particularly advantageous for synthesizing moisture-sensitive materials, such as sulfates, that require low-temperature synthesis conditions. Moreover, they can serve as a safer alternative to hazardous reagents, especially in the synthesis of fluorinated materials. Both sulfate- and fluorine-based materials are promising candidates for future positive electrode materials due to their high working potentials and low costs, which help offset the higher costs associated with ILs and DESs.

3.5 Design of hybrid materials for enhancing conductivity and stability

In most reported works on synthesis involving ILs or DESs, the resulting product is washed with a proper solvent to get rid of a maximum of residual chemical species at the surface of the particles to avoid any possible electrochemical hindrance. In fact, the assumption that residual IL at the surface of the active material would be detrimental to electrochemical performance is not necessarily true, as it was shown by Olchowka *et al.*⁴ with the comparison of the electrochemical performance for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$ obtained by solid-state, ionothermal and solvothermal methods. The ionothermal method consisted of a topotactic reaction between $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and NaF^{41} and resulted in a $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$ material with an homogeneous ionic liquid-based coating on the particle surface, as clearly characterized by TEM imaging, infrared and X-ray photoelectron spectroscopies. The three obtained powders exhibit the same chemical composition but different particle morphologies, which can directly influence electrochemical performance. Nevertheless, it is interesting to note that electrochemical impedance spectroscopy revealed an electrical conductivity for the ionothermally made material (NVPFO₂-IL) higher of more than one and two order(s) of magnitude compared to the materials obtained by solvothermal synthesis and solid-state reaction, respectively. Besides, the electrical conductivity of NVPFO₂-IL starts to decrease upon heating at temperatures higher than 240°C, which was attributed to the ionic liquid layer degradation. Subsequently, the electrical conductivity of NVPFO₂-IL measured upon cooling becomes similar to that of the material obtained by solid-state synthesis, clearly confirming the benefits of an IL coating on the transport properties. This result is in line with previous work of Barpanda *et al.*^{78,79} who reported that IL coating strongly increases the ionic conductivity for lithium metal sulfate fluoride solid electrolyte materials. Additionally, plating/stripping tests

performed in a symmetric cell made of two Li metal electrodes separated by the IL-coated inorganic electrolyte undoubtedly demonstrate that the IL-based coating conducted Li^+ ions.

Theoretical calculations conducted by Choi *et al.*⁸⁰ also confirmed that the presence of 1-butyl-3-methylimidazolium tetrafluoroborate on the surface of $\text{Co}(\text{OH})_2$ particles favors the proton adsorption/desorption processes in aqueous electrolyte. These results were in line with experimental tests conducted by the same group and showing both enhanced rate reversible capacity and long-term stability compared to a $\text{Co}(\text{OH})_2$ powder without functionalized surface. Subsequently, Olchowka *et al.* have also demonstrated that the IL coating of $\text{Co}(\text{OH})_2$ protects the material from oxidation under air storage or moisture, revealing another benefits of such surface modification¹⁸. Thus, this IL layer can be seen as an artificial SEI layer which can greatly improve material stability and electrochemical performance.

Another interesting option is to proceed to a calcination of this ionic liquid layer to generate a carbon coating as it can result in the formation of an homogeneous and graphitized layer, as it was reported in the work of Men *et al.*⁸¹. In comparison, mainstream carbon sources, such as glucose in this example, give thicker heterogeneous carbon films, which is not ideal for cations conduction. Besides, the I_D/I_G intensity ratio observed by Raman spectroscopy is lower for the ionic liquid-based carbon coating (i.e. 0.89 versus 0.99), indicating a higher graphitization degree (less defects), and potentially leading to a higher electronic conductivity. In the end, the IL-based carbon coated LFP exhibits a higher rate capability and capacity retention. More recently Minart *et al.*⁸² also compared the energy storage performance of a $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$ (NVPFO₂) with a 1-Ethyl-3-methylimidazolium tetrafluoroborate surface layer and its carbonized derivative with a N-doped carbon coating (Figure 8). Their investigations revealed better rate capability along with smaller charge transfer resistance for the latter, showcasing also the relevance of such approach for polyanionic electrode materials.

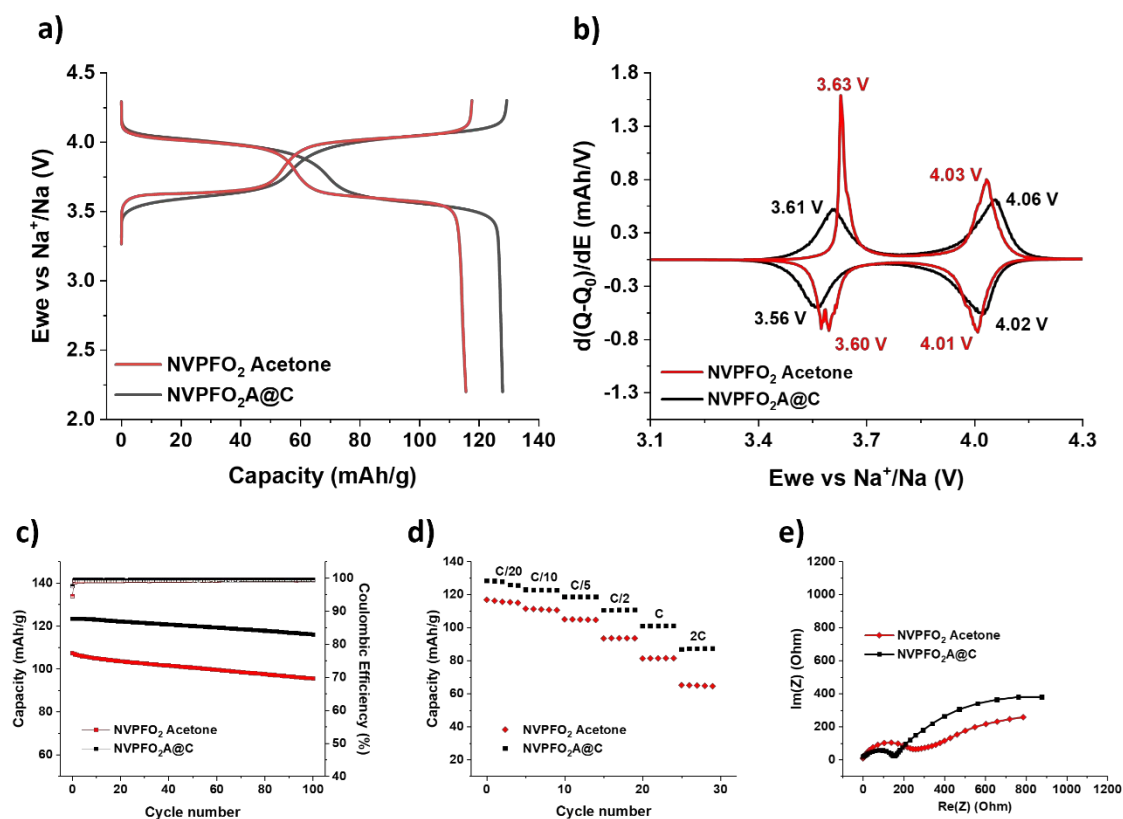


Figure 8: a) Galvanostatic curves of the 3rd cycle obtained at C/20 for NVPFO₂ Acetone (IL-coated) and NVPFO₂A@C (carbon coated), b) Potential derivative curves of the 3rd cycle at C/20 for NVPFO₂ Acetone and NVPFO₂A@C, c) Capacity retention and coulombic efficiency at a rate of C/5 for 100 cycles, d) Capacity retention at different C-rates and e) Nyquist plots obtained for both NVPFO₂ Acetone and NVPFO₂A@C using EIS conducted after 3 galvanostatic cycles at C/20. Reproduced with permission from [82]. Copyright 2025 Elsevier.

Additional works can be cited such as the controlled synthesis of Na₃V₂(PO₄)₂F_{3-y}O_y in a green deep eutectic solvent composed of a mixture of choline chloride, citric acid, and water.⁸³ Whereas the electrode material was nearly electrochemically inactive as obtained after the solvothermal synthesis, most probably due to the residual DES at the particle surface, its annealing leads to a carbon coated material showing excellent performance even at 10C in full cell⁸³. Microscopy analyses revealed the presence of a thin and very homogenous carbon coating, which most probably is at the origin of such good performance. Similarly, the study on Na₃V₂(PO₄)₂F₃ (NVPF) synthesis in deep eutectic solvent by Zhao *et al.*⁸⁴ led to the obtention of mesoporous microspheres structure. Nitrogen BET analysis indicated that the pristine material possesses a specific surface area of 18.15 m²/g, which is relatively high considering that carbon coated NVPF materials exhibit comparable values^{85,86}, where the SSA is mainly

attributed to the carbon layer. It was suggested that the reason for the formation of the porous structure is ascribed to the strong hydrogen bonding network of the solvent along with the reduced evolution of CO₂ bubbles during the reduction process, thereby highlighting the advantages of DESs. Furthermore, the addition of an amorphous fluorocarbon coating, introduced via post annealing with PTFE microspheres at 600°C under argon, gives to this material an outstanding rate capability, with a specific capacity up to almost 100 mAh/g at a rate of 50C.

To conclude this last section, ILs and DESs can play roles beyond that of mere synthesis solvents, as they may also become integral components of battery materials in the form of protective or ion-conductive surface layers. Another possibility is their transformation into carbon coatings when enhanced electronic conductivity is required for proper material operation, as exemplified by the case of polyanionic materials, which can exhibit improved properties (e.g., N-doped carbon coatings) compared with those obtained from conventional carbon sources. In such scenarios, where the solvent is partially or fully incorporated into the positive electrode material composition, the chemistry, properties, and composition of the solvent must be considered not only during synthesis but also in terms of their evolution and impact upon electrochemical cycling. While this integration can enhance material performance, it may also introduce additional challenges if not properly controlled.

A summary table (Table 1) provides an overview of the literature discussed in this second part of the review.

Table 1: Summary table of the reported synthesis of battery electrode materials using ILs or DESs as a (co-)solvent

<i>Medium</i>	<i>Material</i>	<i>Synthesis</i>	<i>T (°C)</i>	<i>Pros (+) / Cons (-)</i>	<i>Ref</i>
<i>Imidazolium-based ILs</i>	<i>LiFePO₄</i>	<i>Ionothermal</i>	<i>250°C</i>	<i>(+) Morphology tunability, low temperature, high crystallinity</i>	<i>17</i>
<i>Imidazolium-based ILs</i>	<i>LiMnPO₄</i>	<i>Ionothermal</i>	<i>220-250°C</i>	<i>(-) Not competitive synthesis</i>	<i>28</i>
<i>1-R-3-methyl imidazolium NTf₂</i>	<i>LiFePO₄</i>	<i>Ionothermal</i>	<i>250°C</i>	<i>(+) Crystallinity control</i> <i>(-) Homemade ILs</i>	<i>39</i>

<i>EMIM TFSI</i>	<i>LiFePO₄</i>	<i>Electrochemically-assisted</i>	<i>275°C</i>	<i>(+) Nanosized particles, film deposition possible (-) IL breakdown due to chlorine species</i>	<i>40</i>
<i>EMIM TFSI</i>	<i>Na₃V₂(PO₄)₂FO₂</i>	<i>lonothermal topotactic</i>	<i>220°C</i>	<i>(+) Solid solution driven mechanism (-) Impurity</i>	<i>41</i>
<i>EMIM TFSI</i>	<i>Na_{2.85}V_{1.6}Mn_{0.4}(PO₄)₂F_{2.4}O_{0.6}</i>	<i>lonothermal topotactic</i>	<i>250°C</i>	<i>(+) Tunable Na content (-) O/F ratio control challenging</i>	<i>42</i>
<i>BMIM BF₄</i>	<i>FeF₃·0.33H₂O</i>	<i>lonothermal</i>	<i>250°C</i>	<i>(+) Safer synthesis path, 100% yield (-) Expensive IL</i>	<i>43</i>
<i>ChCl/urea 1:2 DES</i>	<i>Fe₂O₃</i>	<i>Solvothermal</i>	<i>200°C</i>	<i>(+) Nano-sized particles, cheap synthesis (-) Extensive cleaning required</i>	<i>44</i>
<i>ChCl/EG 2:1 DES</i>	<i>LiMnPO₄</i>	<i>Precipitation</i>	<i>130° – 600°C</i>	<i>(+) Low temperature (-) Extensive cleaning required</i>	<i>45</i>
<i>BMIM Br</i>	<i>Co₃V₂O₈</i>	<i>lonothermal</i>	<i>150°C</i>	<i>(+) Morphology control (-) Expensive IL, long time of synthesis</i>	<i>46</i>
<i>EMIM-Based ILs</i>	<i>Li₃V₂(PO₄)₃/C composite</i>	<i>lonothermal (precursors)</i>	<i>200° – 700°C</i>	<i>(+) Short calcination time (-) High amount of carbon</i>	<i>47</i>
<i>C2-OH DCA IL</i>	<i>LiTiPO₄F</i>	<i>lonothermal</i>	<i>350°C</i>	<i>(+) Nano-sized particles (-) Temperature too high for classic PTFE/Stainless steel autoclaves</i>	<i>48</i>

ChCl/EG 1:2 DES	$Na_3MnPO_4CO_3$	Solvothermal	200°C	(+) Cheap synthesis (-) Extensive cleaning required	49
[CNPIIm][NTf ₂] IL	TiO ₂ /C composite	Ionothermal	50°C – 600°C (pyrolysis)		50
ChCl/Urea 1:2 + water	V ₂ O ₅ (precursor)	Solvothermal	180° – 500°C	(+) Morphology tunability, cheap solvent (-) Pressurized synthesis media due to water	51
[C ₁₂ mim]Br	LiNi _{0.5} Mn _{1.5} O ₄ (precursor)	Co-precipitation	RT	(+) Limited concentration of IL (-) Expensive IL, limited recycling due to low concentration	52
Bmim BF ₄	MnF ₂ as precursor for LiMn ₂ O ₄ and Mn ₂ O ₃	Solvothermal	160°C	(+) IL used as a fluorine source (-) High amount of water inducing pressure	53
1-Alkyl-3- methylimidaz olium bromide	(β (III)-H _x CoO ₂)	Co-precipitation	RT	(+) High specific surface area (-) Difficult to control the chemical composition	55
HPy BF ₄	0.5Li ₂ MnO ₃ ·0.5LiNi _{0.5} Mn _{0.5} O ₂ (precursor)	Co-precipitation	180°C	(+) Limited concentration of IL (-) Limited recycling due to low concentration	57
Pyr ₁₄ TFSI	Li ₃ V ₂ (PO ₄) ₃ /C composite (precursor)	Solvothermal	80°C	(+) Limited concentration and cheap IL	58

				(-) Limited recycling due to low concentration	
<i>EMIM TFSI</i>	<i>LiFeSO₄F</i>	<i>Ionothermal</i>	<i>300°C</i>	(+) Cheap IL and precursors (-) Cleaning in dichloromethane	61
<i>EMIM TFSI</i>	<i>Na_{2.4}Fe_{1.6}(SO₄)₃</i>	<i>Ionothermal</i>	<i>300°C</i>	(+) Cheap IL and precursors (-) Electrochemistry inferior to the materials made by solid-state	65
<i>BMIM BF₄</i>	<i>FeF₃·0.33H₂O</i>	<i>Ionothermal</i>	<i>50°C</i>	(+) Super low temperature (-) Vacuum treatment necessary	69
<i>EMIM BF₄</i>	<i>Na₃V₂(PO₄)₂F₃</i>	<i>Solvothermal</i>	<i>110°C</i>	(+) IL used as a fluorine source (-) Use of GO expensive	70
<i>BMIM BF₄</i>	<i>FeF₃·0.33H₂O/GNS composite</i>	<i>Ionothermal</i>	<i>80°C</i>	(+) Super low temperature	72
<i>BMMIM BF₄</i>	<i>Fe₂F₅/Graphene composite</i>	<i>Ionothermal</i>	<i>50°C</i>	(-) Expensive carbon source	73
<i>BMIM H₂PO₄</i>	<i>Sulfur/Graphene composite</i>	<i>Ionothermal</i>	<i>180°C</i>	(+) Higher specific area compared to water-based (-) Thorough milling step required	74
<i>1,2dimethyl-3-(3-hydroxypropyl)imidazolium dicyanamide</i>	<i>LiVPO₄F/C composite</i>	<i>Ionothermal</i>	<i>320°C</i>	(+) Controlled morphology and particles size	75

				(-) Homemade IL and washing with dichloromethane	
1,2-dimethyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide	$Na_2Fe_xMn_{1-x}PO_4F$	Ionothermal	270°C	(+) Better electrochemical performance than solid-state based products (-) precursors preparation done in glovebox	76
BMIM BF_4	$Co(OH)_2$	Ionothermal	80°C	(+) Easy synthesis and excellent energy storage performance (-) Absence of control on the IL coating amount	80
BMIM $N(CN)_2$	$LiFePO_4@C$	Ionothermal	180°C	(+) Thin and uniform carbon coating (-) IL loss, consumed for the coating	81
EMIM BF_4	$Na_3V_2(PO_4)_2FO_2$	Ionothermal	220°C	(+) Morphology control by topochemical reaction (-) Insufficient carbon coating	82
ChCl : Citric acid : water (3:1:3) DES	$Na_3V_2(PO_4)_2F_{3-x}O_x$	Solvothermal	200°C	(+) Morphology control, uniform carbon coating (-) O/F ratio control to optimize	83
ChCl : EG (1:2) DES	$Na_3V_2(PO_4)_2F_3$	Solvothermal	120°C	(+) Uniform carbon coating (-) PTFE calcination can generate HF	84

4. ILs/DESSs-based synthesis relevance for practical applications

Although most of the published papers on battery material synthesis are based on scientific works carried out at a lab scale and with a lot of attention paid to electrochemical performance, the reality of the industrial world may not be compatible with the proposed synthesis processes. Indeed, those consisting of multiple steps, long heating times, extreme temperature and pressure conditions or expensive reagents must be avoided to obtain the cheapest product possible. To this day, there is no existing large-scale practical utilization of DESs or ILs as synthesis media. Several factors can explain the current situation, some of the main drawbacks highlighted by Binnemans *et Jones*⁸⁷ are as follows: solvents high viscosities, difficulties of recycling, lack of practical demonstrations on a pilot scale and high costs.

At present, the most widespread synthesis pathways in large-scale production of positive electrode materials are the co-precipitation and the solid-state (or ceramic) methods or a combination of both^{88,89}. Both synthesis routes are easily up scalable thanks to their simplicity of procedure and mass production potentials. Concerning solid-state reaction, it basically consists of mixing solid reagents together and heating the mixture at high temperatures under a controlled atmosphere. The process is simple to manage and for some materials, allows to easily obtain targeted stoichiometries by carefully paying attention to the precursor's quantities, with in addition the absence of by-products at the end of the reaction. However, it can be highly energy consuming due to the necessity to reach high temperatures, in some cases for a long time, without mentioning the fact that an intimate and homogeneous mixture of the precursors is more than recommended⁹⁰. Moreover, this process is more likely to provide larger and uneven sized particles, not always allowing to reach the optimum potential of the material.

On the other side, the co-precipitation process has the advantage of providing better control over the particles size, morphology and chemical homogeneity at the atomic scale, through the adjustment of parameters such as pH, temperature, and solution concentration. In some cases, the active material precursors (often called PCAM for cathode material) are obtained through such soft chemistry approach before being mixed and annealed with a lithium or sodium source at medium-high temperatures to get the electrode active materials. Here, the homogeneity of the obtained mixture and the intimate contact between the primary particles due to their smaller and regular size allow to reduce the synthesis temperature and time in comparison to a classic solid-state reaction⁸⁹. The two aforementioned synthesis methods are today well established in the literature and in the chemistry industry for large-scale material production. Consequently, it can be complicated to compare them to ILs/DESSs-based syntheses that are more recent and

still at experimental/development stages. Still, the comparison with solvothermal (including hydrothermal) synthesis can give a realistic idea of the feasibility of the use of ILs and DESs for practical applications.

First, solvothermal synthesis offers similar advantages as co-precipitation, such as homogeneous and controllable morphology and high crystallinity. It is often considered that solvothermal synthesis consumes a reduced energy quantity compared to solid-state reaction thanks to lower synthesis temperatures, but this statement will depend on the targeted phase and the synthesis conditions. In addition, *in situ* surface coating allows extensive material customization⁹¹. This method can be divided into two different specific operating processes: batch and continuous reaction (Figure 9). The first one consists of conducting the synthesis in a sealed autoclave, limiting the produced quantities in time depending on the autoclave volume and the reaction time, making this option potentially limited for industrial applications if the size of the autoclave is not large enough. The other possibility is the continuous reaction method, which this time allows an uninterrupted production flow that is more suitable for large-scale positive electrode material production. However, this solution is more complex to be implemented, because it necessitates faster reaction kinetics that can be reached by increasing the temperature or heating rate. Consequently, continuous solvothermal syntheses are mostly conducted in supercritical conditions. Although they are promising and of big interest, they required in-depth optimization to face several issues, such as high pressure management and possibly reduced material performance because of a fast nucleation rate and the presence of defects⁹¹.

As mentioned, the solvothermal synthesis may not be always energy saving, as it was highlighted by Benedek *et al.*⁹² in the case of hydrothermal synthesis of LiFePO₄, because the large water heat capacity (4184 J.kg⁻¹.K⁻¹ at 20°C) requires a higher energy consumption to heat the reactor in comparison of the ceramic method. To reduce the energy expense per gram of obtained LiFePO₄, the proposed solutions were to lower the reaction temperature and increase the precursor concentration. Notwithstanding, the use of solvents with smaller heat capacities would be beneficial on this aspect, such as ethylene glycol (2433 J.kg⁻¹.K⁻¹ at 25°C), which impact and cost can be diminished by reutilization or recycling⁸⁸.

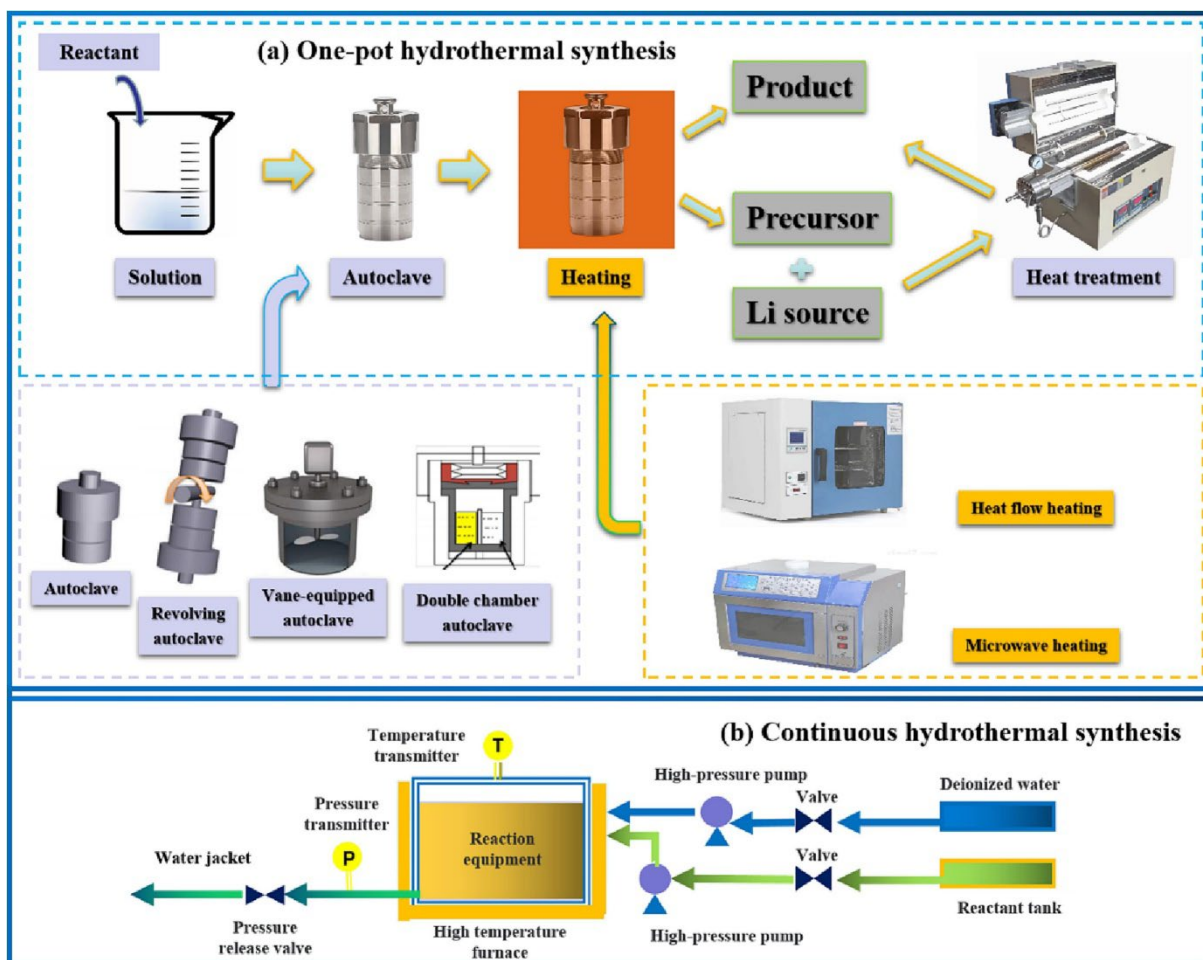


Figure 9. Schematic representations of a) a one-pot hydrothermal synthesis and b) a continuous hydrothermal synthesis. Reproduced with permission from [91]. Copyright 2025 Elsevier.

ILs and DESs can possibly have even lower heat capacities, which would lower the synthesis energy consumption. For example, the 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI) has a heat capacity of $521 \text{ J.mol}^{-1}.\text{K}^{-1}$ ($1331 \text{ J.kg}^{-1}.\text{K}^{-1}$) at $20 \text{ }^\circ\text{C}$ ⁹³ while the choline chloride : urea (1:2) DES exhibits a heat capacity of $181.4 \text{ J.mol}^{-1}.\text{K}^{-1}$ ($2095 \text{ J.kg}^{-1}.\text{K}^{-1}$) at $30 \text{ }^\circ\text{C}$ ⁹⁴. Furthermore, these solvents show a remarkable microwaves absorption ability thanks to their good ionic conduction⁹⁵⁻⁹⁷. Consequently, it could be interesting to take benefits of this characteristic for microwave-assisted ionothermal synthesis in a continuous process because of the possible fast heating rate, resulting in reactions with high yields and giving well crystallized powders^{95,98}. Such scaling-up of microwaves assisted processes although challenging, especially if the solvent used for a continuous flow reactor is highly viscous⁹⁹, already exist for the synthesis of ceramics such as BaTiO_3 or TiO_2 . Then, the remaining issue would be the cost. It is widely assumed in the literature that ILs and DESs can be recycled¹⁰⁰, which would potentially reduce the costs.

Concerning recycling, it is actually more complex for ILs than for other solvents because of their low vapour pressure, which prevents recovering by distillation. Several solutions can be employed depending on the composition of the solvent and on the nature of the post-process impurities. Recham *et al.*¹⁷ recovered various ionic liquids after the ionothermal synthesis of LiFePO₄ by first washing the resulting solution with concentrated HCl to dissolve remaining powder traces. Then, the solution was washed with deionised water to eliminate hydrochloric acid before being mixed with dichloromethane (CH₂Cl₂) to separate the aqueous phase. Finally, the ionic liquid was purified from the CH₂Cl₂ by evaporation, resulting in a recycled solvent with a 90% yield and 200 ppm of water. Despite the great success of the procedure and the possibilities of improvement, it clearly appears that such operation would be costly as well as energy and resources consuming. Thus, the best equilibrium must be found between the solvent and its recycling costs and the difficulty to implement the recovering step within a large-scale material production while also considering the performance or quality gain for the obtained materials.

Regarding DESs, the issue of recycling can be even more complex, potentially limiting their overall sustainability despite their reputation as greener solvents. Indeed, DESs are actually a mixture of minimum two components that are weakly bonded to each other by hydrogen bonding, where ILs are constituted of anions and cations strongly interacting by ionic bonding¹⁰¹. Determining which type of solvent is easier to recycle efficiently is not straightforward, due to the wide variety of components and applications, as highlighted by Alfonso *et al.*¹⁰². Some methodologies do exist and one of the most common for DESs recycling is the antisolvent addition where another liquid (e.g. water, ethanol, acetone...) is added in large quantities in the DES after being used and will cause the precipitation of the remaining solid impurities by breaking the hydrogen bonds network between the HBD and HBA. The DES can then be recovered by evaporating the antisolvent. While this approach is relatively simple and scalable, its main drawback is the high energy consumption required to remove the antisolvent after precipitation.¹⁰³ Additionally, depending on the synthesis, some solid impurities may not be soluble in conventional solvents. Alternative recycling strategies include recrystallization, solid-liquid or liquid-liquid extraction, and distillation¹⁰³.

To conclude on this part, the application of ILs and DESs is, as synthesis media, is still currently limited to the lab-scale although proof-of-concept studies have reported their numerous benefits. For long time, their large-scale use has been limited by their elevated price and difficulties in terms of implementation. Besides complementary complete lifecycle assessment

with upscale estimations are required to evaluate the relevance/benefits of such synthesis approach. Notwithstanding, when comparing both solvents, a large advantage is given to the DESs which are mostly less expensive and more environmentally friendly¹⁰⁴. For comparison, the choline chloride : urea (1:2) DES would cost approximately 56 \$/kg in reagents at a lab scale, while the price of EMIM TFSI can go from 560 \$/kg to 1620\$/kg depending on the purity, manufacturer and purchased quantities.

4.1 Environmental aspects and other applications of ILs and DESs

The production and use of both families of solvents can have a huge environmental impact that must not be neglected^{105,106}. However it is interesting to point out that several studies highlighted that DESs are generally less toxic to (in)vertebrates and aquatic life compared to ILs, even if the toxicity was still existing¹⁰⁷. For example, some tests have been conducted in the literature on aquatic invertebrates and revealed that their exposure to a ChCl : Urea DES would induce morphology changes, but interestingly the solvent seemed to be less toxic than the separated components¹⁰⁸. Moreover, it is important to highlight that for some ChCl-based DESs, their sustainability will be mostly defined by the added HBD: for example glycerol can be bio-sourced, while urea production is mainly coming from fossile fuels¹⁰⁹.

Still, it is important to note that, compared to ILs, DESs are often praised for their simplicity of preparation, as they generally involve just mixing two components, which are frequently already produced on a large scale (e.g., choline chloride). In contrast, ILs typically require complex and energy-intensive syntheses, such as those for methylimidazolium-based ILs, which are widely used in the preparation of inorganic materials. Alternative methods for DES synthesis have been proposed to further reduce the energy footprint, including mechanical milling via twin-screw extrusion instead of conventional high-temperature stirring¹⁰⁹.

Unfortunately, to the best of our knowledge, there is no functioning processing employing ILs or DESs at an industrial scale. Several applications other than synthesis of inorganic materials have been identified for these solvents and their feasibility is still under investigation. One of the most promising is to implement them in (multi)-biorefineries for organic molecules creation, in the same way as it is done today with oil by using for example rice straws or switchgrass¹⁰². However, simulations and tests need to be done to elaborate the first proofs of concept to determine which solvents would fit the best for such process¹¹⁰.

Another interesting application is the electrodeposition of metals. Indeed, ILs and DESs possess a large potential stability window, wider than water for example, preventing hydrogen emission

and/or metal (hydr)oxides deposition at the surface of the coating. Several interesting metals for their properties cannot actually be deposited in aqueous-based solutions baths, or at least not safely, such as aluminium, zinc, titanium or tungsten¹¹¹. They also can easily dissolve metallic species, preventing the use of toxic precursors that are employed for water-based application like in the case of nickel, chromium or cobalt^{111–113}. Nevertheless, it is considered that DESs (or ILs) based electrodepositions would be applicable at an industrial scale only for rare or specific metal / alloy coatings with a high added value, as a lot of metals of interest in the industry are deposited in water-based baths with high efficiencies and low costs.

4.2 Challenges for the application of ILs and DESs as solvent for battery material synthesis

Research and development priorities for the effective application of ILs and DESs as synthesis media for battery materials should focus on three main challenges. First, the cost and sustainability of production can be improved by generalizing the use of bio-sourced or non-toxic precursors, simplifying and optimizing synthesis routes, and scaling up production processes. In this context, the most complex and expensive ILs reported in the literature are incompatible with this roadmap, as their synthesis often requires additional or variable steps depending on the composition. By contrast, DESs are more versatile, as their preparation generally involves only mixing precursors; adapting production lines to different solvent compositions requires minimal modification. Second, the high viscosity of ILs and DESs remains a major challenge, particularly for scale-up. Fluidity can be improved by adding co-solvents (e.g., water)^{25,114}, or by adjusting solvent composition, such as alkyl chain length, functional groups, or the HBD/HBA molar ratio in DESs^{30,115}. Moreover, the rapid expansion of AI opens the possibility of predictive machine-learning models to forecast physicochemical properties based on composition enabling the optimization of performance and cost without extensive experimental testing.¹¹⁶ Finally, the recycling and regeneration of ILs and DESs must be fully developed and optimized before industrial-scale implementation to prevent hazardous waste accumulation. Hopefully, the development of these technologies in the future, as well as the creation of partnerships between industrial key players could help to facilitate recycling and waste management by a synergic effect. For instance, leasing schemes for ILs or DESs could delegate the burden of recycling to the solvent manufacturer, as suggested by Abu-Eishah.¹¹⁷ Alternatively, solvents could be sold alongside expertise in recycling and waste management.

The future will be decisive concerning their fate as potential disruptive technologies applied on an industrial scale or as an original tool for academic research. In addition, if the global environmental impact of these solvents eventually comes to a point where the price would be

the only true limitation, one can imagine that legislation and financial advantages could help their deployment.

5. Conclusion and Perspectives

The growing interest in ionic liquids (ILs) and deep eutectic solvents (DESs) as alternative media for materials synthesis has opened a new paradigm in the design of electrode materials for energy storage. Their unique physicochemical properties—such as high thermal stability, wide electrochemical windows, low vapor pressure, and tunable viscosity and polarity—allow for precise control over particle morphology, size and even composition. As shown throughout the state-of-the-art review, ILs and DESs have demonstrated significant potential in directing growth, promoting anisotropic shapes, stabilizing metastable phases, and facilitating low temperature topotactic and ionothermal reactions, often unattainable with conventional solvents. Beyond morphology control, ILs offer significant advantages for synthesizing moisture-sensitive (e.g. Fe²⁺-based or sulfate compounds) or thermally unstable materials under mild, often anhydrous conditions. Furthermore, the possibility to perform synthesis at moderate temperatures with a reduced risk thanks to the non-existent ILs/DESs vapour pressure, in contrary to classical solvothermal synthesis, is very attractive.

ILs and DESs can also be used simultaneously as solvent and reactants. For example, fluorinated ionic liquids can generate fluorine *in situ*, eliminating the need for hazardous reagents like hydrofluoric acid, particularly in the synthesis of (nano)fluorinated phases. Besides, both types of solvent can functionalize the particle surface, altering surface chemistry and material properties. Such *in situ* surface functionalization by ILs can also be beneficial to electrode or electrolyte materials by bringing plasticity, thus reducing resistance at grain boundaries and enhancing the materials ionic conductivity. Moreover, ILs and DES-derived coatings formed during the synthesis can be converted into homogeneous and thin carbon coating, promoting the material electronic conductivity and enhancing its rate capacity and prolonged cycling stability. ILs can also facilitate the integration of active materials within carbonaceous templates such as graphene, enhancing conductivity and active materials stability—critical factors for high-performance batteries and supercapacitors.

Although ILs and DESs enable the synthesis of innovative and high-performing materials for electrochemical energy storage, further understanding is needed regarding how solvent nature influences particle morphology. This knowledge would allow a shift from trial-and-error approaches to more predictive synthesis strategies, accelerating the development of

optimized materials. Additionally, while surface functionalization of inorganic compounds by ILs or DESs has been experimentally observed, the underlying reaction mechanisms remain poorly understood. Although its impact was reported as beneficial, enhancing material stability or ionic conductivity but for instance its stability during cycling and its impact on the electrode/electrode interphase nature remains a mystery. Therefore, considerable research is still required to elucidate the precise role of surface modification on the performance and longevity of electrode and electrolyte materials.

Finally, compared to well-established methods like solid-state and co-precipitation techniques, synthesis in ILs and DESs media faces limitations including solvent's complex recycling procedures, elevated costs, and limited large-scale demonstrations. Moreover, the elevated viscosities of ILs and DESs make them difficult to operate, and their subsequent sticking nature could require extensive washing to obtain pure and well-cleaned powders. This would not be necessarily a problem for battery materials, as the IL or DES layer can be transformed into a carbon coating, but it would mean a partial solvent loss for each synthesized batch.

Their possible use as synthesis medium for the synthesis of electrode or electrolyte material is still far from a potential large-scale development. To move beyond academic interest and toward industrial relevance, a holistic approach must be adopted, one that balances material performance, cost, scalability, and environmental impact. Moreover, coupling experimental work with artificial intelligence could prove valuable for optimizing synthesis pathways and identifying the most suitable solvent systems for the targeted preparation of specific materials. Ultimately, the transition of ILs and DESs from niche laboratory solvents to mainstream industrial media will depend not only on technological advancements but also on economic incentives and sustainable lifecycle management.

Data Availability

No new data were created or analyzed in this study. Data sharing is not applicable to this article

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