

Metal-Organic Frameworks and Porous Polymer Network-Based Matrices as Nonflammable Battery Electrolytes

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ABSTRACT

Rechargeable Lithium and Li-ion batteries can fail violently when subjected to an internal electrical short, are overheated, crushed, or when they are overcharged/overdischarged. Due to these failures, improvements in safety are urgently needed for Lithium and Li-ion batteries with the use of electrolytes based on nonflammable, room temperature ionic liquids. In this technology and product development effort, *framergy* and Texas A&M University will develop ionic liquid incorporated modified Metal-organic Frameworks (MOFs) and Porous Polymer Networks (PPNs) to serve as efficient electrolyte systems for Li-ion batteries. *framergy*'s novel class of MOFs and PPNs can provide ionic liquids with an ordered structure improving their ionic conductivity while lowering their activation energy.

Keywords: li-ion batteries, nonflammable, ionic liquid, metal-organic frameworks, porous polymer networks

1 SIGNIFICANCE

Due to their high energy densities, low self-discharge rates and low maintenance requirements, Lithium ion (Li-ion) batteries represent the preferred battery format, especially when compared to other rechargeable cells such as Ni-Cad and NiMH batteries. However, in order for Li-ion batteries to be effectively utilized for any application, their safety concerns need to be addressed.

Li-ion battery safety issues typically relate to the thermal stability of the constituent materials. Li-ion batteries are thermodynamically unstable and the compatibility of the battery components is kinetically attained with the presence of the surface passivation films on the electrode surface. The decomposition of this solid electrolyte inter-phase (SEI) layer, resulting from the electrochemically reductive decomposition of the electrolyte on the graphite anode, can initialize exothermic reactions between the lithiated graphite anode and the electrolyte. When a cell is heated above a certain temperature, exothermic chemical reactions between the electrodes and the flammable electrolyte can occur and lead to an increase of the internal cell temperature.

Therefore, Li-ion batteries are very sensitive to thermal and overcharge abuse and pose significant fire hazards. The overcharge of Li-ion batteries can lead to chemical and electrochemical reactions between battery components, gas release, and a rapid increase of the cell temperature. The overcharge can also trigger self-accelerating reactions in the batteries, which can lead to thermal runaway and possible explosion due to the use of flammable electrolytes.¹⁻²

To address these safety concerns, nonflammable ionic liquids (ILs) have gained interest recently. Although the results of studies on ILs revealed that ILs can be used as promising electrolytes³⁻⁶, further improvements are necessary. These improvements directly affect the key performance parameters for lithium batteries and include increased conductivity and lower activation energy. If ILs can be formed into an ordered structure and their ion conductive path can be regulated, the performance of the IL-based batteries can be further improved while leveraging their safe, green and nonflammable attributes. This poses a significant challenge since the effective pinning the counteranions to enhance the dissociation and diffusion of lithium ions requires precise tuning of several different properties of ordered structures in tandem, such as pore size, framework topology, surface area, and interaction with guest molecules.

framergy's novel class of Metal-organic Frameworks (MOFs) and Porous Polymer Network (PPNs) materials can provide ILs with an ordered structure improving their ionic conductivity while lowering the half-cell activation energy. MOFs and PPNs are novel physisorptive materials, which exhibit versatile properties in synthesized matrices.⁷⁻⁸ In this ongoing technology and product development effort, *framergy* in collaboration with Texas A&M University (TAMU) has been testing the feasibility of using MOFs and PPNs-based ionic liquid composites as potential solid state electrolytes for Li-ion batteries. Current activities focus on the optimization of ILs incorporation into MOFs and PPNs with the goal of enhanced diffusion of lithium ions. *framergy*'s product development plan aims demonstrating this novel electrolyte's ionic conductivity, low activation energy, with high rate capability (>20C) across the military operating temperature extremes while documenting the electrochemical performance of the half-cells. The feasibility analysis of the technology will be completed by presenting

the experimental data, following, *framergy* will mainly focus on utilizing this technology in an Air Force/ICBM on-demand power application followed by refining the transition plan and business case analysis.

2 OBJECTIVES

Despite the promise seen in the use of ionic liquids-based electrolytes for safe lithium-ion battery operation, significant room exists for improvements in the following areas of ILs-based electrolyte industrialization. Specifically, two areas of improvements have been investigated with the goal of developing an equivalent or better energy and power density capability in relation to current high-rate Li-ion technology:

Based on work to date, FSI-based ionic liquids, especially $\text{PYR}_{14}\text{TFSI}$ formed by N-n-butyl-N-methyl-pyrrolidinium cation [PYR_{14}^+] and N,N-bis(trifluoromethanesulfonyl) imide anion [TFSI^-] with the lithium N,N-bis(trifluoromethanesulfonyl) imide (LiTFSI) as dissolved lithium salt is identified as a good choice as an IL-based electrolyte.¹⁻³ However, the performance can be improved by effectively pinning the [TFSI^-] anions⁹, this would increase the dissociation and diffusion of lithium ions and improve the overall ion conductivity of the electrolyte. Use of Metal-organic Frameworks (MOFs) with open metal sites to suppress the motion of [TFSI^-] anions to create a conductive path for the lithium ions has been investigated as the first improvement area.

The majority of the published MOFs in the literature don't have the physical and chemical stabilities as they utilize low valent transition metals (TMs).⁷⁻⁸ Physical and chemical degradation of an electrolyte matrix made of such MOFs would eliminate all the advantages of an ordered structure and adversely affect the performance. However, *framergy's* MOFs are highly stable as they are synthesized by high valent TM ion incorporation through CONEKTICTM. CONEKTICTM is a commercial designation trademarked by *framergy*, for Kinetically Tuned Dimensional Augmentation (KTDA) method.¹⁰ The KTDA method is an efficient and robust synthesis method which produces stable MOFs containing high-valence TM ions such as Fe^{3+} , Al^{3+} and Cr^{3+} . Over the course of a series of National Science Foundation (NSF) funded activities (NSF Contracts: 1632486 and 152005), *framergy* has developed a scaled up CONEKTICTM synthesis system and optimized its conditions to lower the cost of its MOFs to achieve commercial viability. This proposed work has leveraged the results of all these activities and transferred the know-how acquired to optimize the best MOF/ionic liquid matrix to serve this study's objectives.

To regulate the ion conductive path, in addition to testing MOFs with open metal sites, the use of Porous Polymer Networks (PPNs) with micropores has been investigated to gradually decrease the motion of the [TFSI^-] anions to create

a conductive path for the lithium ions. This new class of nano-engineered, stable, porous organic polymer based materials⁷ are composed of hypercrosslinked polymer networks, which are insoluble in conventional solvents and exhibit radically high thermal and chemical stabilities.

3 TECHNICAL APPROACH

3.1 IL Composites as Nonflammable Solidified Ion-Gel Electrolytes

Composites are materials that exist as physical mixtures two or more distinct chemical species. These composite materials contain all the benefits of their component parts as well as synergistic effects that lead to improved properties over their constituent components. For battery electrolytes, lifecycle is of the utmost concern. Traditional battery electrolyte solutions, usually solutions containing organic carbonates, are often volatile and flammable, adding safety concerns on top of lifecycle concerns. Composite materials with traditional battery electrolyte solutions have been studied for battery applications because the partner component, often a solid polymer, allows for the encapsulation of the electrolyte, limiting the electrolyte volatility while still allowing for electrical conductivity. Ionic liquids (ILs) have several advantages over traditional electrolyte solvents, chief among them are their low volatility and flammability. However, their high viscosity liquid state hinders their development as functional materials. In addition, while ILs are generally considered to be non-volatile, that is not an entirely correct assertion, as many ILs do exhibit non-zero vapor pressures.

Many IL composites use a solid material (silicas, MOFs, and polymers) as the composite partner, improving the handling and fabrication of battery components using them in addition to preventing leakage due to volatility. When utilizing porous materials, the available pores and channels should still allow for high ionic conductivities. Ionic liquid conductivities when confined in porous matrices have been shown to be comparable to neat IL when at sufficiently high loading. Additionally, the composite matrix still imparts some stabilizing effect even at those loadings. While a matrix material might only interact with the IL molecules adsorbed on the surface, this interaction will still be felt by neighboring IL molecules, forwarding the composite interaction towards the bulk material.

3.2 MOFs-based IL Composite Electrolytes

There are two main possible synthetic routes towards Ionic Liquid incorporated Metal Organic Frameworks (IL@MOFs): ionothermal and direct impregnation. Ionothermal synthesis of IL@MOFs works by the directly synthesizing MOFs in ionic liquid mixtures. However, this method requires that the MOF synthesis is compatible with

the ionic liquid. In addition, it has been seen that IL@MOFs formed in this method end up with the cationic and anionic components separated by the MOF structure. Further, the component that is complementary to the MOF framework, the IL anion, is incorporated in a cationic MOF.

Direct impregnation is an umbrella term for a number of related synthetic methods, such as wet impregnation, capillary action impregnation, and in-situ ionic liquid synthesis. The advantage these methods have over ionothermal syntheses is that they are all post-synthetic incorporation methods. Wet impregnation and capillary action impregnation are both based on contacting the separately synthesized MOFs and ILs, either with a solvent or neat, while in-situ ionic liquid synthesis involves producing the ionic liquids from neutral components after they have been loaded into the MOF structure.

In order to eliminate issues relating to MOF size and crystallinity, MOFs developed using the KTDA method¹¹ has been utilized (KTDA - commercially referred to as CONEKTIC™). The KTDA method is a robust method for producing large particle size MOFs by utilizing preformed MOF clusters. Amongst the series of KTDA MOFs, the iron based PCN-250 has been proven to be a stable and reliable MOF system that maintain high levels of porosity and crystallinity under a variety of working conditions (Figure 1).

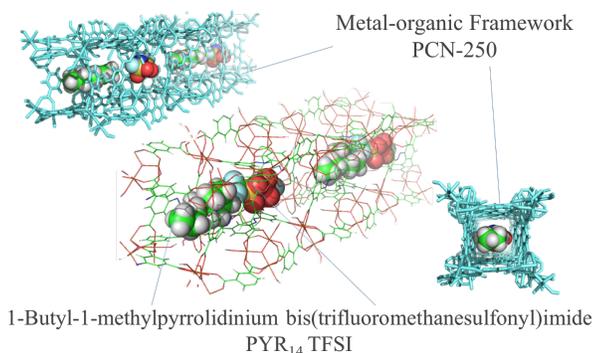


Figure 1: Simulated structures of IL@MOFs showing an ionic liquid encapsulated in the channels of PCN-250 MOF

Another avenue of IL incorporation is through the covalent attachment of IL type components into MOFs. Typically, this is done via incorporation of functional groups on a ligand and either post-synthetically replacement of the original ligand with the modified ligand or forming the MOF using a mixture of the modified and unmodified ligand. It is likely that high levels of IL incorporation are required to achieve effective composites.

A further avenue that is currently being explored is the post-synthetic incorporation of tethered ionic functionality using either the framework or ligand based open metal sites as binding centers. Porphyrin MOFs, such as PCN-222, have

become increasingly common because they can take advantage of the porphyrinic metal center with its open metal coordination site to bind substrates and allow for catalytic transformations. These open metal sites also represent ideal bonding sites for ionic liquid groups because they do not require extensive post-synthetic modification. By pairing the metal center with the correct ligand, a strong binding interaction can be achieved.

Many MOFs contain open metal sites in their secondary building units (SBUs), and recently researchers have also looked into the production of mesopores into traditionally microporous MOFs. These hierarchical porous materials allow for a high level of open metal sites in MOFs which can conceivably bind IL functionalized ligands. Bound IL systems can improve the longevity of these IL@MOF systems as there is less of a chance for the IL molecules to diffuse out of the MOF.

In a related effort, *framergy* is currently investigating the use of its MIL-125NH₂ MOFs in battery applications, specifically in lithium-sulfur batteries for polysulfide shuttle control (Figure 2). Lithium-sulfur (Li-S) batteries are one of the most promising alternative power sources which are promising candidates for next generation of safe and cost-effective high-energy density batteries for mobile and stationary applications. However, Li-S cells suffer from poor cyclability, capacity loss and self-discharge. The underlying cause of the voltage drop and capacity loss during cycling is the irreversible transport of active materials, namely polysulfide shuttle effect. MOFs with nitrogen-containing groups, such as amines possess strong affinity for LiS-polysulfide species and they can be utilized to suppress the polysulfide shuttle, paving the way for commercialization of next generation batteries in portable mobile devices and electric vehicles.

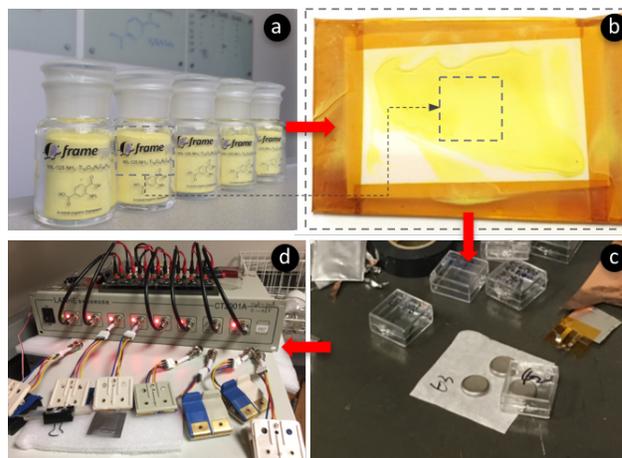


Figure 2: MOFs-based Li-S battery showing the coating of *framergy*'s (a) MIL-125NH₂ (Ti-MOF) on a Celgard membrane (b), button/coin type battery cell assembly (c) and testing in a Landt battery test system (d)

3.3 PPNs-based IL Composite Electrolytes

Porous polymer networks (PPNs) are a subset of porous organic materials that take advantage of the robust nature of the carbon-carbon and carbon-main group bonds. PPNs have a distinct advantage over MOFs due to their high stability, whereas MOFs are oftentimes sensitive to acidic or basic conditions, PPNs are generally stable to chemical etching. Amongst *framergy*'s new class of PPNs, the PPN-150 series, have an additional advantages over other porous materials due to their cheap synthesis. The PPN-150 series is a series of mesoporous melamine-formaldehyde polymers (mPMFs) that are produced from the commodity chemicals melamine and formaldehyde. The materials contain a high nitrogen content which adds a slight level of polarity to the polymers. This polarity, can in turn, be used to aid the tethering of functional materials in the system. The different members of the PPN-150 series are characterized by their incorporated dopants, functionalized small molecules that do not participate in the polymerization; but instead act as additional functional groups in the final polymer that can affect the chemical and physical properties of the material.

As amorphous polymers, the PPN-150 series have a range of porosities, with some pores within the microporous regime ($<20\text{\AA}$) and some in the mesopore range ($20\text{-}500\text{\AA}$). However, the materials are tunable to a degree, with micropores or mesopores dominating the polymer depending on the synthesis conditions. In addition, the PPN-150 series polymers are produced as a single monolith. This allows for a form fitting fabrication within a cell. This monolith can then be doped with ILs post-synthetically without destroying the monolith. This monolith system could feasibly reduce issues resulting from a lack of interparticle communication that could become apparent from loose powders used in a similar set-up.

When incorporating ionic liquids into the PPNs series, wet impregnation route has been followed. This has ensured that the IL seeps fully inside the pores. As the material is mesoporous, the bulk of the IL has not directly interacted with the polymer, but has instead acted as a bulk IL. This material would therefore has the advantages of bulk ILs for their conductive properties, but would be able to be processed and handled like a solid material due to the PPN acting as a case for the IL.

4 CONCLUSION

The anticipated results of this study will help develop a novel generation of Li-ion batteries with improved, nonflammable electrolyte technology. These batteries can demonstrate improved safety under various abuse/extreme conditions while also increasing the battery performance at military relevant operating temperatures, storage temperatures, and at high charge/discharge rates. In tandem with battery development activities, *framergy* is continuously improving its MOFs and PPNs from a cost reduction point. These

activities should also help reduce the acquisition costs of these alternative batteries to levels that will make them cost competitive with existing Li-ion, lead-acid, nickel-cadmium, and Lithium Thermal military batteries in terms of acquisition and life cycle.

REFERENCES

- [1] Balducci, A.; Jeong, S. S.; Kim, G. T.; Passerini, S.; Winter, M.; Schmuck, M.; Appetecchi, G. B.; Marcilla, R.; Mecerreyes, D.; Barsukov, V.; Khomenko, V.; Cantero, I.; De Meazza, I.; Holzapfel, M.; Tran, N., Development of safe, green and high performance ionic liquids-based batteries (ILLIBATT project). *Journal of Power Sources* **2011**, *196* (22), 9719-9730.
- [2] Damen, L.; Lazzari, M.; Mastragostino, M., Short communication. *Journal of Power Sources* **2011**, *196* (20), 8692-8695.
- [3] Johnson, K. E., What's an Ionic Liquid? *The Electrochemical Society Interface* **2007**, *16* (1), 38-41.
- [4] Zhou, Q.; Henderson, W. A.; Appetecchi, G. B.; Montanino, M.; Passerini, S., Physical and Electrochemical Properties of N-Alkyl-N-methylpyrrolidinium Bis(fluorosulfonyl)imide Ionic Liquids: PY13FSI and PY14FSI. *The Journal of Physical Chemistry B* **2008**, *112* (43), 13577-13580.
- [5] Randström, S.; Montanino, M.; Appetecchi, G. B.; Lagergren, C.; Moreno, A.; Passerini, S., Effect of water and oxygen traces on the cathodic stability of N-alkyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide. *Electrochimica Acta* **2008**, *53* (22), 6397-6401.
- [6] Randström, S.; Appetecchi, G. B.; Lagergren, C.; Moreno, A.; Passerini, S., The influence of air and its components on the cathodic stability of N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide. *Electrochimica Acta* **2007**, *53* (4), 1837-1842.
- [7] Lalonde, M.; Bury, W.; Karagiari, O.; Brown, Z.; Hupp, J. T.; Farha, O. K., Transmetalation: routes to metal exchange within metal-organic frameworks. *Journal of Materials Chemistry A* **2013**, *1* (18), 5453-5468.
- [8] Brozek, C. K.; Cozzolino, A. F.; Teat, S. J.; Chen, Y.-S.; Dincă, M., Quantification of Site-Specific Cation Exchange in Metal-Organic Frameworks Using Multi-Wavelength Anomalous X-ray Dispersion. *Chemistry of Materials* **2013**, *25* (15), 2998-3002.
- [9] Fujie, K.; Ikeda, R.; Otsubo, K.; Yamada, T.; Kitagawa, H., Lithium Ion Diffusion in a Metal-Organic Framework Mediated by an Ionic Liquid. *Chemistry of Materials* **2015**, *27* (21), 7355-7361.
- [10] Feng, D.; Wang, K.; Wei, Z.; Chen, Y.-P.; Simon, C. M.; Arvapally, R. K.; Martin, R. L.; Bosch, M.; Liu, T.-F.; Fordham, S.; Yuan, D.; Omary, M. A.; Haranczyk, M.; Smit, B.; Zhou, H.-C. **2014**, *5*, 5723.