

Renewable Fuel for a Generation of Green Batteries

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FEBRUARY 2025

doi.org/10.33548/SCIENTIA1158

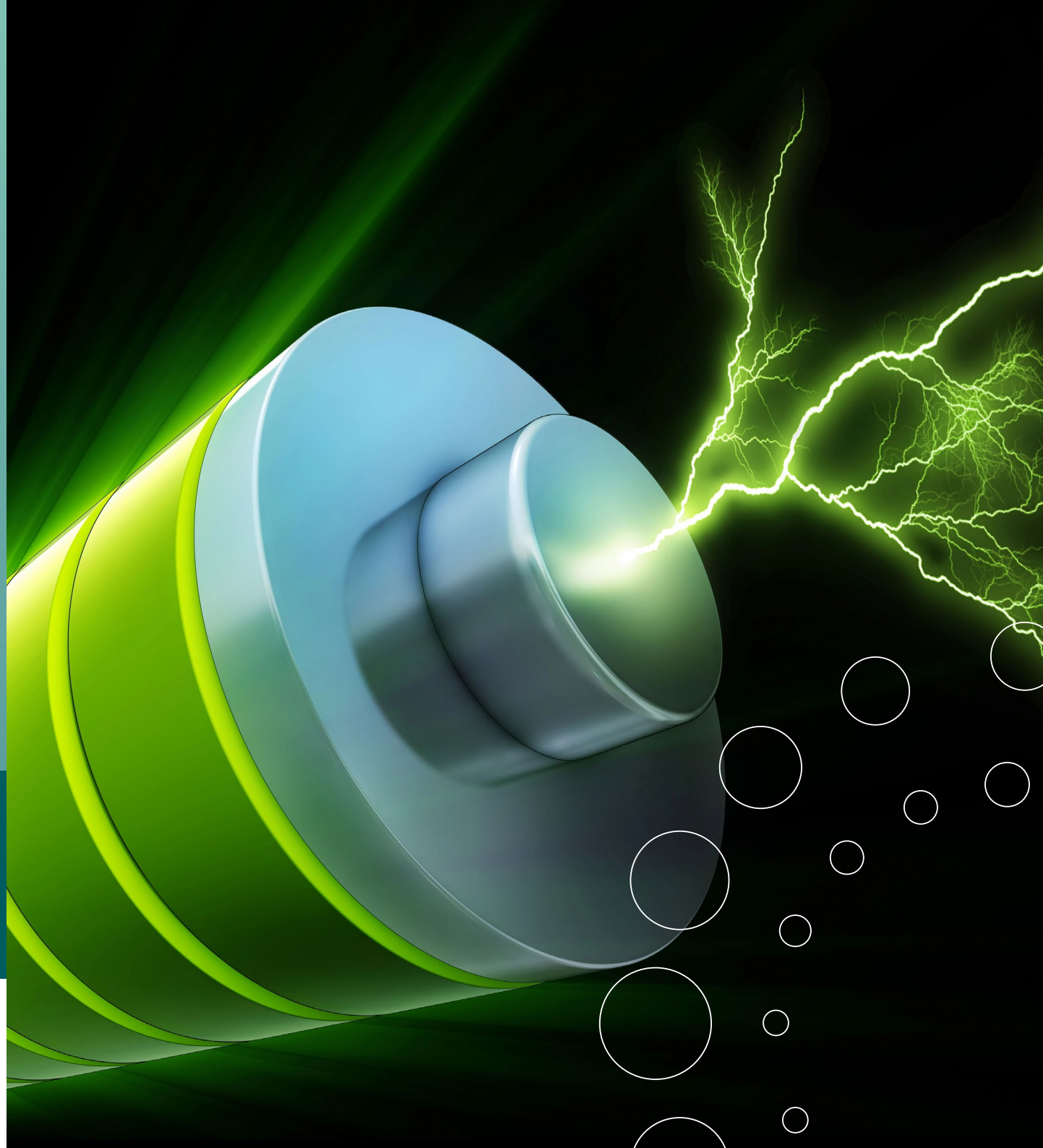


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Renewable Fuel for a Generation of Green Batteries

Revolutionizing energy production has been integral to combatting climate change and reducing our dependence on limited natural resources, but complementary advances in energy storage have been lacking. Dr Thomas Guarr and Dr David Hickey from Michigan State University lead their team in investigating a counterintuitive molecular mechanism which could support a wave of green, renewable, and cheap batteries. If practical, this technology might be the crucial leap towards an entirely green energy system.

Non-aqueous Redox Flow Batteries

As climate change and dwindling resources loom, the world moves towards green and renewable energy. Though steadily successful, these efforts must be mirrored in the development of green and renewable energy storage. The battery technology integral to our power grids has, therefore, become a major research focus. Non-aqueous redox flow batteries (NRFBs) are a promising renewable, environmentally friendly, and cheap alternative to the predominant lithium-ion battery.

As with other batteries, NRFBs are comprised of two chambers containing negatively and positively charged particles, or electrolytes, respectively. The charge difference between chambers fuels an electrical circuit through which energy can be stored or extracted. NRFBs replace standard electrolytes like lithium with what are called redox-active organic molecules (ROMs). ROMs are synthesized from renewable sources, and when the positive and negative electrolytes are linked together in what is termed a 'symmetric battery', only a $\sim 2\$/\text{m}^2$ separator is needed to divide the chambers, replacing $\sim 800\$/\text{m}^2$ selective membranes.

Pyridiniums as Redox-active Organic Molecules

Though promising, NRFBs do face one crucial issue. ROMs must be dissolved in a solvent to circulate and transfer electrons effectively. Solutions with high ROM concentration optimize battery power and efficiency. ROM structure can be customized with molecular additions to increase the maximum concentration at which they will dissolve, but these additions can also increase the viscosity, or thickness, of the solution. This, too, limits how well ROMs can circulate.

Dr Thomas Guarr and Dr David Hickey of Michigan State University and their team have investigated a class of ROMs called

pyridiniums as a resolution to this problem. Positively charged pyridinium ions attract negatively charged tetrafluoroborate ions (BF_4^-), forming an ionic salt. When dissolved in an acetonitrile solvent, this salt can serve alone as a negative electrolyte or linked with a positive electrolyte to fuel a symmetric NRFB. Pyridiniums are promising candidates for use in NRFBs as they retain electrical charges well, exchange electrons readily, and diffuse rapidly throughout the solution.

Investigating Pyridinium Solubility

The team synthesized a range of pyridiniums, each with slight differences in structure, dissolved them in acetonitrile solvent, and compared their solubilities. They used a device called an ultraviolet-visible spectrophotometer to measure how these solutions absorbed certain light wavelengths. With these data, researchers could determine how soluble each pyridinium variant was. Against expectations, even very similar molecules differed widely in solubility. What's more, there were no apparent structural variations which accounted for these differences.

Usually, two factors contribute to how soluble a molecule is. First, how strongly molecules attract each other, as energy is required to overcome these attractions for dissolution. Second, how strongly the molecules attract or repel the surrounding solvent. Computer modelling of pyridinium variants revealed no clear trends between these forces and solubility.

The researchers then turned to X-ray crystallography for a clearer picture of how pyridinium molecules interact. They grew pyridinium crystals, then fired X-rays at them and analyzed how the rays scattered to build an image of the crystal structure. Through this method, they found that the molecules interact primarily through their ionic interactions with BF_4^- , but these forces also bore no relationship with solubility.

CH- π Interactions

One difference could be found, which correlated with solubility. This was the presence or absence of CH- π interactions between molecules. These are weak attractive forces between carbon-hydrogen bonds on one pyridinium molecule and the electrons of another. This relationship is counterintuitive, not only because these attractive forces are so weak but also because it seems that attraction between pyridiniums somehow increases their solubility, which is the complete opposite of what would be expected.

How could this be? As the researchers explained, 'we considered the possibility that CH- π interactions may disrupt electrostatic interactions during the assembly of pyridinium salts near their solubility limit'. Dr Guarr and Dr Hickey reasoned that CH- π interactions draw pyridinium molecules into pairs with enough force to disrupt the wider organization of molecules into an ordered crystal structure. This disruption makes pyridinium crystals less tightly bound together and, therefore, more easily dissolved. In this model, they see a more nuanced mechanism by which ROMs can be made more soluble, allowing for powerful and efficient NRFBs without the drawbacks of increased ROM viscosity.

Pyridinium Characterization

With their model and a diverse library of pyridiniums, the team sought a more thorough understanding. Researchers used a technique called cyclic voltammetry to pass an electric current through solutions of dissolved pyridiniums. By studying differences in electrical conductivity, they were able to characterize the electrochemical properties of 23 pyridinium variants. Of these 23, they selected four pyridiniums with limited, moderate, or extensive CH- π interactions.

These four variants were then investigated further. They found that solutions containing these molecules exhibited exceptionally low viscosities even at high concentration, a promising property for use in NRFBs. These solutions conducted electrical current well, and that conductivity increased linearly with pyridinium concentration. High-concentration ROM solutions usually require significant amounts of another supporting electrolyte to maintain conductivity without increasing viscosity too greatly. However, it seems that these low-viscosity, high-conductivity pyridiniums would not need large amounts of supporting electrolytes to operate effectively in NRFBs.

These results are instrumental in the confirmation of pyridiniums' potential as NRFB ROMs. In the words of researchers, this pyridinium library 'demonstrates robust electrochemistry, practical viscosities, and high conductivities in acetonitrile that further promote their candidacy as an anolyte for organic non-aqueous energy storage applications'.

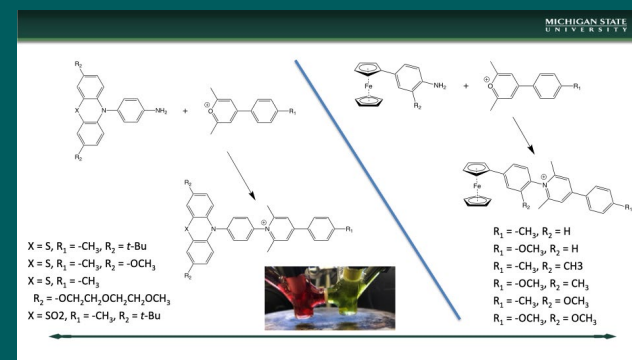
Finding the Optimal Conditions for Pyridinium ROMs

These results seem to confirm that pyridiniums could prove effective materials for use in green and renewable NRFBs, demonstrating both high electrical conductivity and favorably low viscosity in solution. Dr Guarr and Dr Hickey, therefore, sought to push further with their research, intending to narrow down the conditions required for optimal performance of these ROMs.

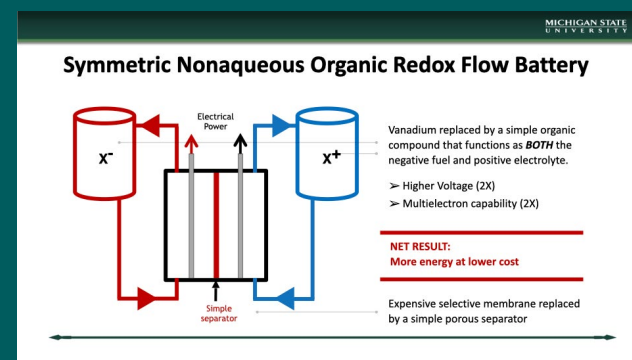
Researchers first tested the solubility of the four selected pyridinium variants in acetonitrile solvent spiked with a small amount of water. They found that trace water, in fact, increased pyridinium solubility. This confirmed the importance of ensuring



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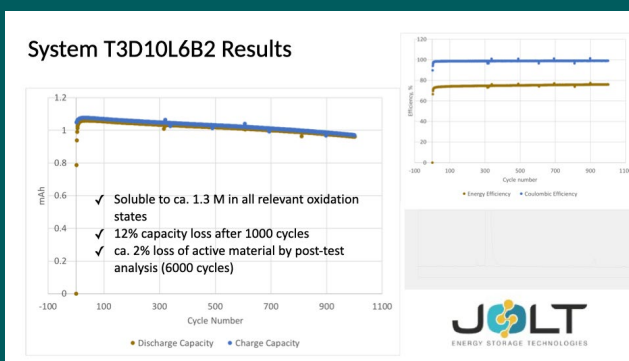
△ Credit: Thomas Guarr.



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Dr Guarr and Dr Hickey highlight the need for an expansion of approaches that consider dispersion-based interactions to produce molecules with particular physical characteristics.



^ Credit: Thomas Guarr.

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a pure acetonitrile solvent in future experiments for a fair comparison of pyridinium solubilities. Further, this finding could prove instructive when implementing pyridinium solutions in future NRFBs within power grids.

The Effect of Temperature

Another variable condition that affects ROM solubility is temperature. Determining how temperature influences maximum ROM concentration in solution is essential to optimizing the power density of NRFBs. The team found a linear relationship between increased temperature and increased solubility for all four pyridinium salts regardless of structural variation. They were also able, by comparing these relationships between the salts and by taking into account the relative strengths of CH- π interactions, to determine the exact role pyridinium-pyridinium pairing played in solubility.

Specific formulae were determined that linked the number of CH- π interactions between pyridinium molecules with the energy values associated with solvation. In this way, the solubility of any pyridinium variant could be predicted given the energy supplied, such as through increased temperature. These formulae could constitute the theoretical basis on which pyridinium-based NRFBs might become a widespread practical reality.

A Model Linking CH- π Interactions and Solubility

It was also during this research that the fundamental model of how CH- π interactions influence pyridinium solvation was clarified. According to this model, pyridinium molecules that cannot form CH- π interactions or can form just a single interaction with another molecule, organize themselves into tight, structurally

uniform crystalline structures which require large amounts of energy to be disrupted and dissolved. Those pyridinium variants that can form two or more CH- π interactions organize into what are termed 'self-complimentary dimers', pairs of two identical molecules. These pairs hinder the formation of tightly packed crystalline structures, decreasing the energy needed for dissolution.

Researchers also determined that three or more CH- π interactions allow for increasing numbers of possible configurations for these self-complimentary dimers. With more numerous configurations comes a greater degree of disorder throughout the greater crystal structures, and so a lowered energy threshold for solvation. As opposed to an intuitive model, here is a case where increased molecule-to-molecule interaction actually weakens the overall structure of the substance, increasing solubility.

Onwards and Upwards for Renewable and Green Technologies

This is by no means a concluded line of research. Dr Guarr and Dr Hickey highlight the need for an expansion of approaches that consider dispersion-based interactions to produce molecules with particular physical characteristics. They see a link between CH- π interactions and solubility as an unexplored bridge between molecular structure and other consequential physical properties.

According to the researchers, 'employment of larger temperature ranges, temperature-solubility studies with varying solvent, and temperature-stability studies are recommended as potential avenues for future directions in this research'. Ultimately, the results of the team's work have cut a clear path towards NRFBs based on pyridinium ROMs that are not only renewable and green, but also powerful, efficient, and reliable enough to assume a major role in our energy grids.

MEET THE RESEARCHERS



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Dr Thomas Guarr is the Director of Research and Development at the Michigan State University Bioeconomy Institute. He runs the Organic Energy Storage Laboratory where he works to help combat climate change by developing redox-active organic compounds for use in electrocatalysis and energy storage. The laboratory's projects include the fabrication of supercapacitors based on conductive metallophthalocyanine polymers and the development of organic batteries. Dr Guarr earned his PhD in chemistry from the University of Rochester in 1984 and has since worked with various universities and companies to further his research. In 2014, he cofounded Jolt Energy Storage Technologies to develop and commercialize his work. He has co-authored numerous scientific publications and holds over 75 patents.

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Dr David Hickey is Assistant Professor at the Michigan State University Department of Chemical Engineering and Materials Science. He runs the Hickey Laboratory, which focuses on molecular engineering at electrochemical interfaces for applications in energy storage, catalysis, and biosensing. His work aims to develop technologies to address the problems of large-scale energy storage and the sequestration of greenhouse gases. Dr Hickey received his PhD in Chemistry from the University of Oklahoma in 2014, after which he worked as a Postdoctoral Fellow and Research Assistant Professor at the University of Utah. He has authored over 80 scientific publications and five book chapters, and holds two patents.

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FUNDING

The National Science Foundation, Department of Energy, Ocean Exchange, Shell GameChanger Accelerator™ (GCxN) Powered by NREL, The Community Foundation of Holland/Zeeland, Lakeshore Advantage



FURTHER READING

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