



INORGANIC LIQUID ELECTROLYTES FOR ADVANCED LITHIUM-ION BATTERIES

An innovative pathway forward to the next generation of rechargeable power

Conventional electrolytes have long been recognized as the significant “weak link” in lithium metal and lithium-ion batteries. While there have been significant improvements in the composition, processing, and fabrication of electrode materials over the past twenty+ years, electrolytes remain largely unchanged. Currently, they are composed of light organic fluids – chiefly small molecule compounds known as carbonates. While these fluids do their principal job – that is to transport lithium ions from one electrode to the other – they have some serious weaknesses that engender several major problems. Currently, they are composed of light organic fluids – chiefly small molecule compounds known as carbonates. While these fluids do their principal job – that is to transport lithium ions from one electrode to the other – they have some serious weaknesses that engender several major problems. Chief among these problems are: a) flammability; b) volatility; c) thermal instability; and d) electrochemical instability. All of these problems work simultaneously to cause severe safety problems, to reduce battery useful lifetimes, and to limit the total energy that can be stored in the battery. These severe failings are greatly exacerbated as there is an ever-increasing need for more powerful (energy dense) systems that operate longer, with more reliability and most importantly, much greater safety.

To overcome the failings of conventional organic solvents, New Dominion Enterprises (NDE) has developed a new and improved class of electrolyte materials designed to enable a new generation of lithium batteries – **inorganic fluids**. Unlike other conventional organic liquids, NDE inorganic fluids dramatically increase the safety of the battery as they are non-volatile, non-flammable, and non-toxic. Further, they improve battery useful lifetimes as they are also both thermally and electrochemically extremely robust. Together, these properties make for a powerful leap forward for electrolytes, one that is also conveniently a “drop-in” technology - in that none of the current methods of manufacture and battery assembly will need to be changed in order to accommodate this new inorganic fluid revolution in electrolyte technology.

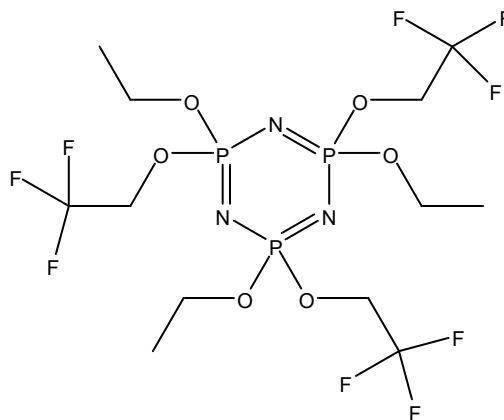


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These NDE inorganic fluids are based upon Phosphorus-Nitrogen chemistry and have been intensively studied

by the inventor, Dr. Mason K. Harrup, for nearly 20 years while working as a Principal Investigator at the Idaho National Laboratory prior to founding NDE. As shown to the right, the inorganic fluid that is the core of these new electrolyte systems is based on a family of compounds known as phosphazenes.



The molecular architecture of the phosphazenes for this electrolyte application has been optimized by NDE and is currently in commercial production under the name Phospholyte[®]. It is precisely this type of inorganic fluid that holds the key to enabling newer, safer, higher energy density batteries to become a reality in the very near term.

NDE's inorganic fluids are superior to other possible alternative electrolytes, namely solid-state materials and ionic liquids. First, since these inorganic fluids are precisely that – fluids – they have much higher lithium-ion mobility than that for true solids affording the ability to operate at higher drain rates than is currently available in solid state materials. Much of the work that actually does exhibit acceptable drain rate behavior of “solid” electrolytes over a nominal temperature range (at least -20 to +50 C) is actually a polymer or other solid scaffolding that has been imbibed with a liquid plasticizer to increase performance. However, though this approach has been shown to have limited utility, it also brings with it the same severe problems associated with all conventional organic fluids – safety, stability to higher voltage operations, and useful lifetimes before degradation, as elaborated further below. Similarly, NDE's inorganic fluids are superior to ionic liquids in several key aspects. Ionic liquids are chiefly organic in nature and as such are also subject to some of the same safety issues as the more conventional organic electrolytes. Further, as ionic liquids possess a formal negative charge in each molecular pair, problems with too high an association energy with lithium ions severely adversely affects the



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performance of such systems. Finally, ionic liquids have a natural tendency towards high self-association energies leading to relatively high melting points and very poor low temperature performance. In contrast, NDE's inorganic fluids are neat fluids that are neutral, not ionic, which exhibit great promise to become a critical electrolyte component for a variety of emerging energy storage technologies.

One very promising opportunity for NDE's inorganic fluids to make an immediate positive impact on such emerging higher energy density systems is in the adoption of lithium metal anodes. The three most significant challenges to the use of Li metal as an anode are: electrolyte solvent stability to lithium metal, overall safety, and dendrite suppression. NDE's new inorganic fluid electrolyte solvents are beneficial in overcoming all three of these issues simultaneously. Further, these inorganic fluids have been proven to make superior electrode/electrolyte interfacial layers through the incorporation of inorganic component(s) within such layers upon formation.

The first of the problems to address as enumerated above is electrolyte solvent compatibility with lithium metal. Complete stability of our inorganic fluids has been conclusively demonstrated. Lithium metal can be stored completely immersed in these inorganic fluids indefinitely (tests ran for ~1 year) with no degradation of the fluid as evidenced via multinuclear NMR (^1H , ^{13}C , ^{19}F , and ^{31}P). Nor was there any effect upon the metallic lithium surface as evidenced by no tarnishing or decomposition layer formed on the metal surface as evidenced via ESEM. Further, cyclic voltammetry experiments have shown conclusively that these inorganic fluids are completely electrochemically stable over a much wider potential range ($< 0.0\text{V}$ to $>5.0\text{V}$) than conventional organic electrolyte solvents. This wider electrochemical window of stability favors extending cell cycle life and calendar life as well as enabling higher rate capability – both during use and especially during recharge times.

The second issue is safety. It is in this area that our inorganic fluids exhibit the best improvement over any conventional electrolyte solvents. Our inorganic fluids are absolutely non-volatile exhibiting negligible vapor pressure at $> 235\text{ }^\circ\text{C}$. As it is the gasses of volatilized



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electrolyte solvents that ignite, our demonstrated significant depression of the vapor pressure at all temperatures of even hybrid organic/inorganic electrolytes ameliorates this problem. Also, our inorganic fluids are also completely non-flammable – no flash point until decomposition > 250 °C. As such, not only will the inorganic component of an electrolyte solvent blend never burn, it has been demonstrated that the flash point of hybrid organic/inorganic electrolyte solvents significantly increases with increasing inorganic character of the hybrid. Having higher flash points make it much more difficult for a flame event to occur – even if the cell housing is breached. Further, in hybrid organic/inorganic electrolyte solvent systems, selective volatilization of the organic component leads to rapidly self-extinguishing electrolyte solvent fluid. With even as little as a few percent (> 3%) of the Phospholyte[®] fluid included in the electrolyte, this self-extinguishing behavior reduces burn times by over an order of magnitude and prevents all of the available organic fuel from being consumed.

The third issue is dendrite suppression. While NDE's inorganic products are fluids and would likely have to be mixed with some percentage of conventional organic fluids in a practical battery, they have demonstrated much higher stability to not only lithium metal but also a greater stability at extreme voltages where conventional organic fluids rapidly decompose. This decreased electrolyte decomposition at the anode surface would reduce physical irregularities from forming at the Li metal surface – particularly during the plating process upon recharge. Prevention of such irregularities leads to a more even, uniform plating of the lithium metal. This aids in the suppression of surface anomalies which should in turn lead to the suppression of one of the main root causes of dendrite formation. In on-going development work, Phospholyte[®] has greatly extended the cycle life (> 75%) vs organic electrolyte solvents before capacity fade exceeds 25%.

Finally, this novel electrolyte material is now available for use and evaluation. NDE's pilot scale manufacturer is now producing multi-kilogram scale production runs and sample lots have been provided to now > 9 pilot efforts with commercial battery companies. To date, while these efforts are still in the early to mid-stages, data on performance and safety have been consistently



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encouraging. These programs are mostly with commercial battery applications, although two are with Defense Department contractors for specialized purposes. Recognizing the potential for demand from the DoD as well as from commercial companies, NDE is now beginning the transition to full-scale (metric ton) manufacturing.

Importantly, since 2021, NDE has been awarded both multiple Phase One as well as multiple Phase Two SBIR contracts. The Phase Two technical efforts are progressing well with firm plans to transition at least some of these efforts into follow-on commercialization opportunities. In addition to this public sector success, several of the private sector endeavors are also yielding positive results, and one principal strategy employed by NDE is to partner with entities that possess or are building gigafactories as the most efficient manner in which to penetrate several vertical markets simultaneously, as these markets are notoriously fractured and disparate. For further information and discussions – please contact us!

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