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Title: Novel Inorganic Liquid Electrolyte Solvents for Lithium Batteries.

One of the most important innovations in the energy world in the last century was the development of the lithium-ion, rechargeable battery in the 1970's. Drs. Whittingham and Goodenough were awarded the Nobel Prize for Chemistry in 2019 for their developments. Since then, while there has been seemingly endless research on the development of new electrode materials seeking to improve energy density and safety, little progress has been made on replacing what is the possibly the single greatest vulnerability of today's lithium-ion batteries, the organic carbonate electrolytes.

While this class of compounds does indeed function, providing for rapid lithium-ion mobility, it suffers from several major drawbacks. First, these compounds are extremely volatile, limiting the useful thermal operational window, potentially causing cell stress from internal cell pressures, and can cause extreme safety hazards. Second, these compounds are highly flammable. This a major root cause in almost all lithium battery fires/explosions. Third, these compounds have a relatively narrow electrochemical window of stability. This limits the voltage operational window, and constrains cell power and total energy density. Fourth, these materials and their decomposition products are known to be toxic. This generates a real need to replace these carbonate compounds if the goal of realizing the true next-generation battery is to be achieved. The obvious solution to realizing these true, next-generation batteries is to **replace these carbonates**, not simply by modifying them as has been the subject of extensive research over the past two decades, but by going to another class of compounds altogether – **inorganic liquids**.

Among the required properties of this inorganic replacement are: (1) thermal stability; (2) electrochemical stability; (3) facile lithium-ion transport; (4) and the potential to be manufactured at a large scale, at a reasonable cost point**.** To achieve this vision, New Dominion Enterprises (NDE) is developing and commercializing novel inorganic liquid electrolyte materials for lithium batteries, that possess all of these properties. Additionally, the first inorganic liquid product has already been successfully manufactured at a commercial pilot scale. Thus, our inorganic liquid is an ideal replacement for the organic carbonate electrolytes now used in lithium batteries. In this first-generation product based upon phosphazenes, the higher inherent viscosity of the inorganic fluid, Phospholyte®, requires that it must be only a partial replacement for the carbonates, yielding the need for co-solvents. It is also noteworthy that NDE is developing a second generation based upon phosphoranimines lowering the molecular weight by two-thirds, thereby reducing viscosity, and a third-generation inorganic fluid that is a 100% replacement for all organic compounds. There are four critical attributes that these new inorganic fluids possess that make them excellent candidate to form the basis of an entirely new electrolyte solvent system – one capable of eventually replacing organic carbonates all together.

1. Thermal Protection – Phospholyte® is extremely thermally stable as it will not volatilize and is completely non-flammable (FP > 250 °C, VP < 10 Torr @ 250 °C). In stark contrast, carbonate electrolytes are not thermally robust. They are also highly volatile and highly flammable. As Phospholyte® is neither flammable nor volatile, this allows batteries to possess a much wider thermal operating range, and significantly increases battery lifetimes.

2. Electrochemical Window Expansion - Typical carbonate electrolytes are electrochemically stable only over an operational range of 0.7-0.8 V. Outside of this window of stability, carbonates self-degrade via complex oxidative and reductive mechanisms. Since the goal of this program is to use lithium metal anodes, this weakness is exacerbated. The inclusion of 20% Phospholyte® in the carbonate mix expands this window of electrochemical stability to nearly 2.0V. This means that the use of Phospholyte® will help provide the electrochemical stability needed in an electrolyte to realize a practical high voltage cell.

3. Safety/Non-propagation - The most serious problem facing the lithium battery industry today is safety, especially in large format applications due to numerous recorded incidents of battery fires/explosions. As the inherent volatility and flammability of the organic electrolytes are the reasons for the safety concerns, inclusion of Phospholyte® make the electrolyte self-extinguishing. As a result, total burn times are much shorter and this prevents cell-to-cell propagation in the inevitable event of a single cell failure. Since cells for larger-format lithium batteries are produced on such a massive scale, it is realistically impossible to believe that there will never be single cell failure. By eliminating propagation, the principal safety issue is neutralized.

4. Improved Solid Electrolyte Interphase (SEI) and Longer Lifetimes All lithium batteries form a protective layer between the electrolyte and the electrodes (the SEI) and this has a large impact on battery performance and lifetimes. Results obtained by NDE during development show that the SEI formed with Phospholyte® has lower impedance than all-organic electrolytes. Further, in lithium metal anode cells, the lithium metal is consumed and re-formed during charge/discharge cycles, forming and re-forming a more stable anode/electrolyte interface is paramount during the lithium plating/stripping process to maintain a uniform deposition, thereby maintaining capacity and perhaps even depressing dendrite growth – a principal failure mechanism in lithium metal cells leading to disastrous safety outcomes.

5. Initial Testing With Lithium Metal Anodes. The two major impediments to the widespread use of lithium metal anodes are: a) the voltage range; and b) the overall safety of the device in a secondary format. Both of these issues are mainly due to the use of organic carbonates. Because Phospholyte® is known to be extremely voltage tolerant as well as possessing superior safety characteristics, to support this assertion that Phospholyte® would enhance both the safety and performance of lithium metal-based cells a preliminary study using lithium metal anode in combination with an NMC cathode was conducted. Results of this preliminary study are very promising. **Based upon the results of this simple testing as well as the arguments presented above, the assertion that Phospholyte® is an excellent candidate to form the basis of a new electrolyte, worthy of significant additional study, in high energy density cells is well founded.**

Speaker Brief Bio: Dr. Mason K. Harrup, Ph.D., received a BS from the University of Virginia and a Ph.D. from Emory University, followed by post-doctoral research performed at Michigan State University. He worked at the Idaho National Laboratory from 1997 until 2014 as a Principal Investigator. There he provided synthetic chemistry expertise for a variety of programs.

He directed development of novel hybrid organic/inorganic materials as electrolyte solvents and additives for advanced lithium batteries. Dr. Harrup has over 60 patents issued and pending, over 80 publications and over 70 presentations in the area of inorganic synthesis and materials science. He’s responsible for scientific support and direction of technical work on all NDE projects, interacts with the technical teams of all commercial evaluators, authors technical proposals for new business and funding opportunities, and is the inventor of liquid inorganic electrolyte materials.