RECHARGEABLE BATTERIES WITH IMPROVED DISCHARGE CAPACITY AT -40 °C TO -60 °C FOR SURVIVING THE LUNAR NIGHT.

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Introduction: Future science missions to the Lunar surface will require hardware, electronics and energy storage systems that can tolerate the extreme low temperatures of the Lunar night. Some missions will require continuous operation through the night and others will only need to tolerate it and wake up and operate at the Lunar dawn. Other mission near the poles may only receive marginal heating from the sun due to shadows and low sun angles.

The temperatures expected (about -180 °C at night, lower in craters, and up to +120 °C in the day) dictate that batteries and electronics currently must be housed in temperature regulated chambers kept between 0 °C and +40 °C, because this is where lithium-ion cells have adequate performance. Automotive electronics are rated down to -40 °C and military electronics are rated down to -55 °C and it would be advantageous to have rechargeable batteries that could work well at least to the same low temperature ranges (either down to -40 °C or -55 °C) to match the limits of existing electronics. In the future, even lower temperature electronics are envisioned and rechargeable batteries that can discharge at -60 °C, -80 °C or even -100 °C would be useful for waking up after the cold Lunar night, or for operating intermittently or continuously during the night.

Although lithium-ion batteries must be charged at temperatures above -20 °C (preferably above 0 °C) to avoid irreversible capacity loss, this is generally not considered a problem for Lunar missions because the batteries are charged during the day and there is enough capacity to survive the night and wake up once they are warmed back up by the Sun and recharged by the solar panels. Typically the battery is sized for descent and landing operations which exceed the capacity required for static operations once on the Lunar surface. But what is still desired is the ability to discharge at extremely low temperatures below -20 °C (to operate science experiments, or generate heat to further warm up the batteries and run other equipment at higher rates of discharge).

There are similar low temperature requirements for electric or hybrid electric aircraft, and arctic exploration instruments on Earth. Thus, there are also terrestrial transportation and science applications of batteries that have better extreme low temperature discharge capacity and specific energy.

Problem: The low temperature performance of lithium batteries is limited by several factors: (1) the conductivity of the electrolyte; (2) the resistance of the solid electrolyte interface (SEI) or the cathode electrolyte interface (CEI); and (3) the charge transfer resistance of the SEI and/or CEI (moving lithium ions into and out of the solid electrodes).

Advances have been made in fluorinated carbonate liquid electrolytes capable of cycling down to -60 °C or lower [1]. These have been demonstrated on other NASA-funded projects and interestingly they promote low temperature lithium plating on the anode, however improvements in capacity retention at extreme low temperatures (-40 °C to -60 °C) are still of interest when considering the needs of operating electronics in the Lunar day-night cycle.

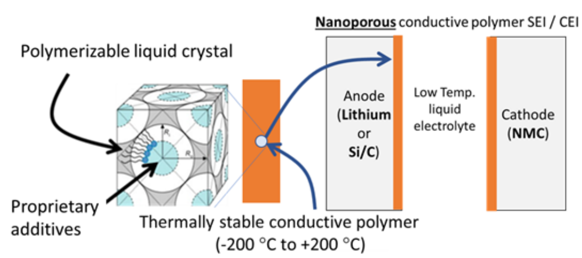
Solid-liquid interfaces in lithium batteries can suffer from slow lithium ion transfer across this boundary, especially when cold. The typical solution to this problem is to add an ionically conductive additive to form an SEI or a CEI *in situ* during cell formation, or to add an artificial SEI / CEI prior to cell assembly to promote lithium diffusion between electrodes and the electrolyte (and to prevent unwanted side reactions). In many cases the artificial SEI / CEI is a polymer. However, the polymers typically cannot perform well in wide temperature ranges expected on the Lunar surface (even for partially temperature-regulated housings or instruments). The materials used for artificial SEI's / CEI's either melt or dissolve when too hot or they become non-conductive when too cold. Advancements that address battery operation at extreme temperatures, combined with high specific energy are still critically needed.

Solution: Our proposed solution to make rechargeable lithium-ion batteries that operate in extreme temperature environments is to develop an artificial SEI / CEI that solves the poor lithium conductivity at the solid-solid interphases in high energy density batteries at -40 °C to -60 °C. The same artificial SEI / CEI also provides some discharge capacity at even -80 °C, but the primary focus of this work is to take full advantage of electronics rated to -55 °C. The polymer artificial SEI / CEI must not melt or degrade at high temperatures and must retain 75% of the room temperature capacity and specific energy of the battery when operated at -40 °C (and still maintain close to half of the capacity at -55 °C). It is also critical to combine and stabilize this modified solid electrolyte/binder with high voltage / high energy density cathodes and anodes to produce the high specific energy batteries to meet NASA's needs.

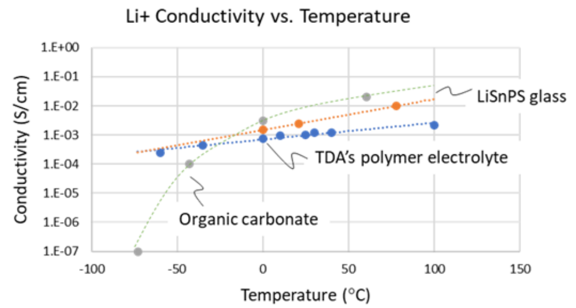
In this project TDA Research is developing and testing a proprietary [2],[3] artificial SEI / CEI for NMC 811 cathodes combined with lithium metal or Si/C anodes.

Our ion conducting polymer has 3-deminstonally interconnected nanopores, a high thermal stability and a higher conductivity at low temperatures relative to traditional polymer electrolytes. This is because our polymer is made by the self-assembly and crosslinking of liquid crystal monomers that form a rigid nanoporous polymer that doesn't melt and that doesn't rely on polymer segmental motions for lithium ion transport at low temperature. The ions transport through the nanopores in a hopping mechanism, like in ceramic conductors.

Illustration and Properties: The technology concept is illustrated below. An artificial CEI is applied to the cathode (and alternatively an SEI also on the anode). A low temperature liquid electrolyte and a conventional separator are used in combination with these artificial interfaces. The result is a significantly improved discharge capacity at -40 °C and -60 °C compared to the same battery cell with no artificial interfaces.



Our artificial SEI / CEI performs well at low temperatures because it has both a high lithium ion conductivity, combined with a very low charge transfer resistance, and it has a temperature vs. conductivity behavior similar to solid ceramic conductors: it has a linear Arrhenius behavior and maintains a high conductivity at low temperatures. In contrast, most other polymer solid electrolytes and liquid electrolytes have a drastic reduction in conductivity below the glass transition (or freezing) temperature. Furthermore, our coating is stable in contact with the low temperature electrolyte during repeated cycling.



Our artificial SEI provides significant improvement in the discharge specific energy as shown in the table below (particularly at -40 °C and -60 °C)

Temperature	Specific Energy Retention (no artificial SEI / CEI)	Specific Energy Retention (with artificial SEI / CEI)
+20 °C	100.0% 740 wh/kg	100.9%
0 °C	94.7%	95.6%
-20 °C	74.6%	84.0%
-40 °C	39.1%	73.8% 546 Wh/kg
-60 °C	5.9%	33.6% 249 Wh/kg

*Results based on C/10 charging at 20 °C and C/10 discharge at the temperature in the table. Lithium metal anode, NMC811 cathode, low temperature ester electrolyte. 100% specific energy is equal to 740 Wh/kg based on the active material weight in the cathode in the control tests with no artificial SEI / CEI. Coin cells are tolerant to cryo-temperature resting in charged state prior to discharge.

Status: Completed an SBIR Phase I project to develop our artificial SEI/CEI and tested coin cells: planning to partner with battery producers for larger cells. Seeking input from Lunar surface instrument and hardware providers on future low temperature battery performance targets.

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References:

[1] Holoubek *et al. ACS Energy Lett.* 2020, 5, 5, 1438-1447.
[2] US Pat. No. 7,931,824
[3] Additional patents pending