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RESEARCH ARTICLE SUMMARY

ELECTROCHEMISTRY

Liquefied gas electrolytes for electrochemical energy storage devices

Cyrus S. Rustomji, Yangyuchen Yang, Tae Kyoung Kim, Jimmy Mac, Young Jin Kim, Elizabeth Caldwell, Hyeeseung Chung, Y. Shirley Meng*

INTRODUCTION: The vast majority of electrolyte research for electrochemical energy storage devices, such as lithium-ion batteries and electrochemical capacitors, has focused on liquid-based solvent systems because of their ease of use, relatively high electrolytic conductivities, and ability to improve device performance through useful atomic modifications on otherwise well-understood solvent molecules. However, with a delicate balance between electrochemical stability, ionic conductivity, temperature, and safety, there has understandably been little change over a number of decades in the electrolyte composition, which consists primarily of carbonate-type solvents and provides limited improvement in device performance.

RATIONALE: It is often assumed that molecules that are gaseous at room temperature are typically nonpolar and have low intermolecular attraction, which prevents them from condensing at room temperature. Although

this may be true in general, there are a number of reasonably polar molecules that are gaseous at room temperature. It is hypothesized that these relatively polar gaseous molecules, when liquefied under pressure, could dissolve salts at room temperature to form liquefied gas electrolytes. Although a number of potential solvents were explored, the present study focuses on the use of hydrofluorocarbons, which are nontoxic and have relatively strong chemical bonds, allowing for a wide electrochemical window. Although these solvents generally have moderate dielectric constants, their exceptionally low viscosity allows for a superior solvent dielectric-fluidity factor that is higher than commonly used solvents, potentially allowing for relatively high electrolytic conductivities. Last, the low melting points of the solvents studied could allow for substantial improvements in device operation at low temperatures. Although they may require modified processes for manufacturability, the pressures of the proposed chemistry are moderate, and the sol-

vents are compatible with commonly used separator and electrode materials.

RESULTS: All tests were conducted in high-pressure vessels in which the solvents were in a liquefied state under their own vapor pressure. We found that electrochemical capacitors that have a liquefied gas electrolyte based on difluoromethane (CH_2F_2) have an exceptionally wide operation temperature from -78° to $+65^\circ\text{C}$, with

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similar resistance and capacitance to conventional devices. Further, we demonstrate an increase in operation voltage to 3.0 V—equivalent to a

23% increase in energy density—under accelerated life conditions. The use of a liquefied gas electrolyte based on fluoromethane (CH_3F) show plating and stripping efficiencies on lithium metal of ~97% over hundreds of cycles under aggressive testing (1 mA cm^{-2} , 1 C cm^{-2} each cycle), with no evidence of dendritic growth. This impressive behavior on lithium metal is thought to be due to the particular combination of an exceptionally low viscosity, high vapor pressure, and LiF chemical reduction products on the anode surface. The same fluoromethane-based liquefied gas electrolyte shows good cycling and rate performance on a LiCoO_2 cathode. We demonstrate a high discharge capacity retention of 60.6% at -60°C , which is thought to be due to an ideal solid electrolyte interphase formed on the electrodes as observed through x-ray photoelectron spectroscopy analysis. Last, we show that there is a substantial drop in electrolytic conductivity at elevated temperatures because of salt precipitation out from solution as the supercritical point is approached ($\sim +40^\circ$ to 80°C) and recovery in the conductivity as the temperature is lowered. This reversible mechanism is demonstrated to effectively shutdown operation in an electrochemical capacitor device and may similarly enable reversible battery shutdown at increased temperatures, mitigating the potential of thermal runaway and improving safety.

CONCLUSION: A succinct background and demonstration of liquefied gas electrolytes for both electrochemical capacitors and lithium batteries are presented and show potential for substantial improvements in low-temperature operation, energy density, and safety. With their superior electrochemical and physical properties, further exploration and development of these liquefied gas solvents is warranted for their use in next-generation energy storage devices and beyond. ■

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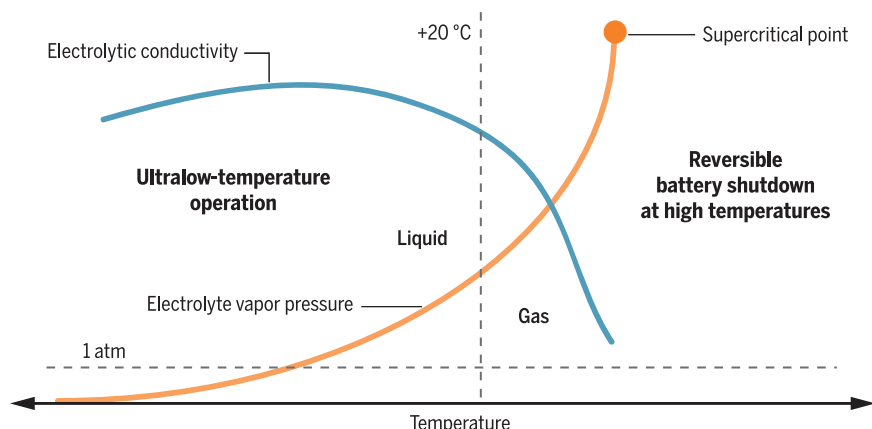


Illustration of the electrolytic conductivity and pressure with temperature of the studied liquefied gas electrolytes. The electrolyte solvent is liquefied from a gaseous state under pressure. Exceptionally high electrolytic conductivities are observed at low temperatures. Further, a sharp drop in conductivity occurs as the salt precipitates near the supercritical temperature, which allows for a reversible shutdown mechanism to mitigate battery thermal runaway.

RESEARCH ARTICLE

ELECTROCHEMISTRY

Liquefied gas electrolytes for electrochemical energy storage devices

Cyrus S. Rustomji,¹ Yangyuchen Yang,² Tae Kyoung Kim,² Jimmy Mac,¹ Young Jin Kim,² Elizabeth Caldwell,² Hyeseung Chung,¹ Y. Shirley Meng^{1*}

Electrochemical capacitors and lithium-ion batteries have seen little change in their electrolyte chemistry since their commercialization, which has limited improvements in device performance. Combining superior physical and chemical properties and a high dielectric-fluidity factor, the use of electrolytes based on solvent systems that exclusively use components that are typically gaseous under standard conditions show a wide potential window of stability and excellent performance over an extended temperature range. Electrochemical capacitors using difluoromethane show outstanding performance from -78°C to $+65^\circ\text{C}$, with an increased operation voltage. The use of fluoromethane shows a high coulombic efficiency of $\sim 97\%$ for cycling lithium metal anodes, together with good cyclability of a 4-volt lithium cobalt oxide cathode and operation as low as -60°C , with excellent capacity retention.

Electrochemical energy storage devices, such as electrochemical capacitors and batteries, are crucial components in everything from communications to transportation. Aqueous-based electrolytes have been used for well over a century, but a substantial increase in the energy density was achieved through the development and use of electrolytes based on organic solvents, which allowed for operation at higher voltages. The modern lithium (Li)-ion battery was only realized with a serendipitous discovery that the use of ethylene carbonate, a solid at room temperature, as an electrolyte solvent could stabilize the graphite anode via formation of a suitable solid electrolyte interphase (SEI) and allow for reversible lithiation and delithiation of the electrode (1). Although the majority of electrolyte work remains with liquid solvents and solid electrolyte systems, there has been very little work using electrolyte solvents that are typically gaseous under standard conditions. Although not used as an electrolyte, sulfur dioxide [boiling temperature (T_b) = -10°C] (2) and sulfuryl chloride fluoride (T_b = $+7.1^\circ\text{C}$) (3) have been used as catholytes in nonrechargeable primary Li batteries; however, both use additional cosolvents in the electrolyte, which are liquid at room temperature. There have also been a number of studies using ammonia (T_b = -33.3°C) as a liquid anode because of its ability to solvate alkali metals (4–6).

It is often assumed that materials that are gaseous at room temperature are typically nonpolar and have low intermolecular attraction, which prevents them from condensing at room temperature or even solubilizing salts in a cooled, or pressurized, liquid state. Although this may be true in general, there are a number of reasonably polar molecules that show low London dispersion forces because of their small molecular size and are gaseous at room temperature. For instance, the dielectric constant of dichloromethane ($\epsilon_{\text{DCM},20^\circ\text{C}} = 8.9$, $T_b = +40^\circ\text{C}$) is substantially lower than that of structurally similar difluoromethane ($\epsilon_{\text{DFM},20^\circ\text{C}} = 14.2$, $T_b = -52^\circ\text{C}$), although at room temperature, the former is a liquid, whereas the latter is a gas. At low temperatures or with moderate pressures, these types of polar gasses may be liquefied and have been shown to be capable of solubilizing salts to form liquefied gas electrolytes, in which ion transport, redox phenomena, and other fundamental studies have been conducted (7–13).

We explored the use of liquefied gas electrolyte systems exclusively composed of solvents that are gaseous at room temperature and atmospheric pressure in rechargeable energy storage systems. Although we evaluated a number of potential liquefied gas solvents, we focused efforts on hydrofluorocarbons, which have moderate dielectric constants that allow for the solubility of salts to form conductive electrolytes. These electrolytes show ultralow-temperature operation, increased energy density in electrochemical capacitors, and high Li plating and stripping efficiency for potential use of the high-capacity Li metal anode in batteries. It should be cautioned that although the hydrofluorocarbon solvents them-

selves are generally nontoxic, they do range from nonflammable to highly flammable, and combustion products may be toxic to humans. Further, these solvents do exhibit a low to high global warming potential. As such, these materials should be handled properly (additional information is provided in the supplementary text).

Physical and chemical properties of liquefied gas solvents

The electrochemical stability for a range of liquid and liquefied gas solvents was qualitatively estimated by calculating the ionization potential and electron affinity of the solvents (fig. S1 and table S1). Selecting from the solvents with optimal electrochemical stability and polarity, we identified six promising liquefied gas solvents, which are compared with conventional liquid solvents in Fig. 1A. In general, these liquefied gas solvents show improved oxidation and reduction resistance compared with conventional solvents. In particular, these calculations suggest fluoromethane and difluoromethane would have improved electrochemical stability over tetrahydrofuran and ethylene carbonate, which are known for their high stability at highly reductive and oxidative potentials, respectively. Electrostatic potential maps are overlaid on the physical structures of these solvents for comparison in Fig. 1B, which may be used as a tool to qualitatively determine the electrochemical reduction stability of solvents. The regions of highest electrostatic potential (Fig. 1B, bluest regions) increases in the order of tetrahydrofuran < fluoromethane < difluoromethane < ethylene carbonate, which correlates well to the high electrochemical reduction stability of tetrahydrofuran and indicates that fluoromethane should similarly have good reduction stability. The regions of lowest electrostatic potential (Fig. 1B, reddest regions) increases in the order of ethylene carbonate < tetrahydrofuran < fluoromethane < difluoromethane, which correlates well with the high solubility for the relatively small Li^+ cation in ethylene carbonate and tetrahydrofuran and indicates that the solubility would be better in fluoromethane than difluoromethane.

The dielectric constant of the gaseous solvents ($\epsilon = 10 \sim 15$) is significantly lower than that of conventional liquid solvents, which may limit their ability to solubilize various salts. However, the room-temperature viscosities of the liquefied gas solvents are also significantly lower than conventional liquid solvents. These properties for the liquefied gas solvents fluoromethane and difluoromethane are compared in Fig. 1C. Both fluoromethane and difluoromethane have a liquid viscosity about three times lower than that of acetonitrile, which is commonly used in high-power devices such as electrochemical capacitors. Because of their exceptionally low viscosities, it is expected that the ion mobility is quite high in electrolytes composed of these solvents. As a qualitative measure of the electrolytic conductivity for a range of solvents, the ratio of dielectric constant to viscosity ($\epsilon_r \cdot \eta^{-1}$), or the solvent dielectric-fluidity factor, is compared in Fig. 1C.

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We found that the liquefied gas solvents have a superior dielectric-fluidity factor compared with conventional liquid solvents, including acetonitrile, which generally shows some of the highest electrolytic conductivities (14). This qualitative comparison demonstrates that relatively high electrolytic conductivities may be expected in these solvents having only moderate dielectric constants. Further, the viscosities of these solvents remain favorable at very low temperatures (fig. S2), which may allow for high electrolytic conductivity at temperatures at which conventional solvents may freeze.

Vapor pressure curves of the six liquefied gas solvents studied over a range of temperatures are moderate and compared in Fig. 1D. Of the solvents studied, fluoromethane and difluoromethane have the highest vapor pressures of 3.8 and 1.8 MPa, respectively, at +25°C. The melting points for each of the solvents are below -100°C. Although the boiling points of these solvents are all below room temperature, the present study uses these solvents while they are liquefied under their own vapor pressure in a hermetically sealed cell, allowing for electrolyte and cell characterization at increased temperatures at which the solvent would normally be gaseous. Further, these solvents have fairly accessible supercritical points, as detailed in Table 1. Having zero surface tension in the supercritical phase, these solvents may provide additional advantages, such as superior wetting or access to nanopores in high-surface-area electrodes (15).

Electrolytic conductivity measurements

Electrolytic conductivity measurements of the liquefied gas electrolytes were conducted in order to determine the most promising solvents. Various liquefied gas solvents and salts were tested over a range of temperatures, and it was found that these electrolytes do not follow typical conductivity versus temperature curves. Generally, the electrolytic conductivity for a liquid electrolyte will scale approximately linearly with increasing temperature because of decreasing solvent viscosity. However, the liquefied gas electrolytes show three distinct regions of conductivity over a wide range of temperatures, as shown in Fig. 2A for 0.1 M TBAPF₆ (tetrabutylammonium hexafluorophosphate) in difluoromethane. The first region at lower temperatures shows the typical increasing conductivity with increasing temperature, which is due to the decreasing viscosity with increasing temperatures ($\eta_{\text{DFM},-60^\circ\text{C}} = 0.31 \text{ mPa}\cdot\text{s}$, $\eta_{\text{DFM},+20^\circ\text{C}} = 0.12 \text{ mPa}\cdot\text{s}$) (16). At moderate temperatures, there is a clear maximum followed by a gradual decrease in conductivity. As the solvent approaches the supercritical point ($T_{\text{c,DFM}} = +78^\circ\text{C}$), a drop in conductivity is expected (17) and occurs because of the decreasing dielectric constant lowering the ion mobility ($\epsilon_{\text{DFM},-57^\circ\text{C}} = 28.2$, $\epsilon_{\text{DFM},+20^\circ\text{C}} = 14.2$) (18, 19). Whereas all solvents generally show a decreasing dielectric constant with increasing temperature, the studied solvents already have a comparably low dielectric constant at room temperature and would be susceptible to con-

siderable ion pairing at increasing temperatures. At even higher temperatures, an abrupt change in the conductivity is observed, which separates the second and third regions of the conductivity curve. Because this sharp change occurs at temperatures considerably lower than the supercritical point, any related phenomena are not thought to contribute to this behavior. It was found that this abrupt change in electrolytic conductivity is concurrent with a sudden increase in the pressure of the electrolyte solution, beyond the normal solvent vapor pressure. This phenomenon may be explained by considering the thermal expansion behavior of the solvent. In practice, nearly the entire volume of measurement cell is filled at a low temperature with liquid solvent, while a small volume remains open, which is naturally filled with gaseous solvent through thermal evaporation. As the temperature increases, the volume of liquid phase increases because of thermal expansion ($\rho_{\text{DFM},-60^\circ\text{C}} = 1.24 \text{ g}\cdot\text{cc}^{-1}$, $\rho_{\text{DFM},+20^\circ\text{C}} = 0.98 \text{ g}\cdot\text{cc}^{-1}$) (16), and the volume of the vapor phase decreases. At an elevated temperature, the thermal expansion of the solvent will cause the liquid phase to occupy the entire volume of the cell, and any further increase in temperature will result in an isochoric increase in pressure due to the compression of the liquefied gas electrolyte. It should

be cautioned that rather high pressures may be observed if solvent thermal expansion is restricted considerably. An increase in pressure on DFM can increase the dielectric constant of the solvent quite dramatically (20). Therefore, it may be understood that the abrupt change in electrolytic conductivity in the third region relative to second region of Fig. 2A is due to an improvement in ion mobility from the increased dielectric constant of the solvent, which results from the increased pressure on the electrolyte system. Although this pressure-induced effect may be generalized to all electrolytes, it is a particularly substantial effect because of the already moderate dielectric constant and high compressibility of this solvent.

Similar electrolytic conductivity phenomena may be observed for the other liquefied gas electrolyte systems explored. The electrolytic conductivity of 0.1 M EMITFSI [1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide] in multiple liquefied gas solvents is shown in Fig. 2B and decreased in the order of difluoromethane, fluoromethane, 1,1-difluoroethane, fluoroethane, 2-fluoropropane, and 1,1,1,2-tetrafluoroethane. This follows the order of decreasing dielectric-fluidity factors for the solvents described in Table 1, which gives credibility to the simple qualitative model proposed (the dielectric constants for fluoroethane and 2-fluoropropane were unavailable in the literature).

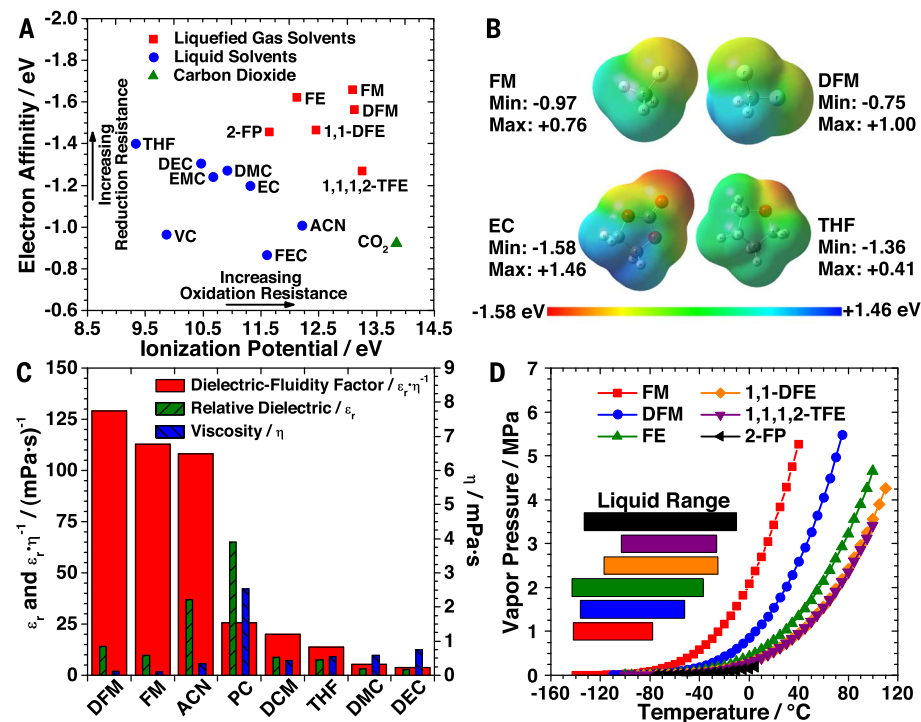








Fig. 1. Physical and chemical properties of liquefied gas solvents. (A) Density functional theory-calculated ionization potentials and electron affinities. (B) Electrostatic potential maps. (C) Relative dielectric, viscosity, and dielectric-fluidity values. (D) Vapor pressure curves with liquid range of various conventional and liquefied gas solvents. Liquefied gas solvents are fluoromethane (FM), difluoromethane (DFM), fluoroethane (FE), 1,1-difluoroethane (1,1-DFE), 1,1,1,2-tetrafluoroethane (1,1,1,2-TFE), and 2-fluoropropane (2-FP). Liquid solvents are acetonitrile (ACN), propylene carbonate (PC), dichloromethane (DCM), tetrahydrofuran (THF), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), ethylene carbonate (EC), vinyl carbonate (VC), and fluoroethylene carbonate (FEC).

Table 1. Physical properties of the liquefied gas electrolytes studied. Vapor pressure, density, relative dielectric, and viscosity values taken as a saturated liquid at +20°C under saturated vapor pressure, except where noted (8, 16, 18, 48–55).

Solvent	Structure	T_m (°C)	T_b (°C)	T_c (°C)	P_c (MPa)	Vapor pressure (MPa)	M wt (g·mol ⁻¹)	Density (g·cc ⁻¹)	Dipole (debye)	Relative dielectric	Viscosity (mPa·s)	$\epsilon_r \cdot \eta^{-1}$ (mPa·s) ⁻¹
Fluoromethane		-142	-78	44	5.90	3.41	34.03	0.599	1.85	9.7	0.085	114
Difluoromethane		-136	-52	78	5.78	1.47	52.02	0.981	1.98	14.2*	0.120	118
Fluoroethane		-143	-38	102	5.01	0.79	48.06	0.707	1.94	—	0.125	—
1,1-Difluoroethane		-117	-24	113	4.52	0.51	66.05	0.912	2.26	12.5†	0.173	72
1,1,1,2-Tetrafluoroethane		-101	-26	101	4.06	0.57	102.03	1.225	2.06	9.7‡	0.207	47
2-Fluoropropane		-133	-9	143	4.20	0.18§	62.09	0.969	—	—	—	—

*20°C and 2 MPa. †24°C. ‡30°C. §0°C. ||-9.4°C.

Because difluoromethane was found to exhibit the highest electrolytic conductivity, various salts were tested in this solvent (fig. S3). It was found that TBAPF₆ exhibited the highest electrolytic conductivity in difluoromethane, and further studies of this electrolyte system were studied with various concentrations of salt (Fig. 2C). There is a considerable increase in the conductivity of the liquefied gas electrolyte from a concentration of 0.02 to 0.50 M TBAPF₆, which shows that the salt has good solubility in difluoromethane despite its relatively low dielectric constant. The electrolytic conductivity of the 0.50 M solution shows a maximum conductivity of 31 mS·cm⁻¹ at +30°C. However, the low-temperature conductivity of 13 mS·cm⁻¹ at -60°C is excellent. Previous work showed the optimization of binary mixtures of liquid-based solvents with close attention to the conductivity, melting points, and potential window and demonstrated a similar electrolytic conductivity at -60°C for 0.75 M TEABF₄ (tetraethylammonium tetrafluoroborate) in acetonitrile: methyl formate 3:1; however, the potential window of this electrolyte was limited (21). At various concentrations, the conductivity curves in Fig. 2C exhibit the same general three regions of electrolytic conductivity across the temperatures measured. A distinct change in the slope of the conductivity curve in the first region, most notably at a concentration of 0.5 M TBAPF₆, is thought to be due to increasing ion pairing, which is expected to occur in these moderate dielectric solvents with high salt concentrations. There is a gradual change in the temperature separating the second and third regions, which increases from +35° to +79°C from a salt concentration of 0.02 to 0.5 M. This may be understood by the lower thermal expansion coefficient of the solution with increasing salt concentration, which would require more thermal energy to

volumetrically expand and create the isochoric increase in pressure, resulting in the abrupt change in conductivity.

Although difluoromethane was shown to have an exceptionally high electrolytic conductivity with many salts, we found that this solvent was unable to solubilize Li salts. This is likely due to the steric hindrance of the highly electronegative fluorine atoms of adjacent solvent molecules preventing formation of a solvation shell around the Li⁺ cation. Further work showed that Li bis(trifluoromethane)sulfonimide (LiTFSI) could only be solubilized in the monofluorinated liquefied gas solvents: fluoromethane, fluoroethane, and 2-fluoropropane. This is in agreement with previous work, which also suggested that these monofluorinated solvents have an increased basicity and binding energy to the Li⁺ cation over difluoromethane (22), and with the previously discussed electrostatic potential maps of the solvents in Fig. 1B. The electrolytic conductivities of these three monofluorinated liquefied gas solvents with 0.1 M LiTFSI are compared in Fig. 2D. Fluoromethane is shown to have the highest electrolytic conductivity of the three solvents, as is expected from the exceptionally high dielectric-fluidity factor. A maximum conductivity of 1.2 mS·cm⁻¹ is seen at -22°C, and an impressive low-temperature conductivity of 1.1 mS·cm⁻¹ is seen at -60°C. For comparison, a low-temperature electrolyte using LiPF₆ in a mixture of carbonates and methyl acetate had an electrolytic conductivity of 0.6 mS·cm⁻¹ at -60°C, but it had relatively poor performance in a full cell because of the nonideal solvent system (23). The electrolytic conductivity at higher concentrations saw little improvement with the LiTFSI salt. At higher temperatures, there is a sudden drop in conductivity due to the precipitation of the salt out of the electrolyte as fluoromethane reaches its critical tem-

perature ($T_{c,FM} = +44^\circ\text{C}$), which is a useful safety feature among Li-based electrolytes.

Electrochemical capacitors

Because difluoromethane shows the highest electrolytic conductivity for non-Li-based salts, we studied the electrochemical stability of this solvent. The cyclic voltammetry curves for 0.1 M TEABF₄ in difluoromethane at both +25°C and -60°C are shown in Fig. 3A. At +25°C, we observed a potential window of 5.70 V. The positive potential limit of 2.47 V versus Pt matches well with that of anion oxidation (7). We observed a substantial reduction current with an onset potential of -3.23 V versus Pt, which results in the continuation of a high reduction current in the reverse sweep direction, possibly owing to corrosion of the working electrode. These potential limits are in good agreement with previous results with a similar salt system (7). At -60°C, the electrolyte shows an impressive electrochemical window of 6.83 V, which is wider than that at +25°C because of slower chemical kinetics at the decreased temperatures.

Commercial electrochemical capacitors of 350 F-rated capacitance were tested with 0.5 M TEABF₄ in difluoromethane and with a standard liquid electrolyte composed of 1 M TEABF₄ in acetonitrile for comparison, both of which were tested under identical mechanical cell conditions and submerged in electrolyte. The capacitance and resistance over a range of temperatures are shown in Fig. 3B. At +25°C, the capacitance for both devices is ~375 F and remains fairly constant over the temperature range studied, with only a small decrease to ~350 F at low temperatures. The resistance of 8.5 and 11.0 milliohms for the difluoromethane and acetonitrile devices, respectively, at +25°C emphasizes the high electrolytic conductivity and applicability of the electrolyte to electrochemical capacitors for

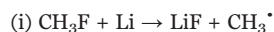
high power applications. At low temperatures, whereas the acetonitrile-based device steadily increased in resistance to 14.9 milliohms at -40°C , just above its freezing point, the difluoromethane-based device decreases in resistance to 5.8 milliohms at -20°C . This is in agreement with the electrolytic conductivity measurements, which show a maximum in electrolytic conductivity around this temperature range. At lower temperatures, the resistance slowly increases yet is still comparable at -78°C and $+25^{\circ}\text{C}$, highlighting the excellent low-temperature performance of the electrolyte. This operation temperature is nearly 40°C lower than commercial acetonitrile-based electrochemical capacitors are rated for and is unsurpassed by other low-temperature electrolyte formulations (24). At an elevated temperature of $+65^{\circ}\text{C}$, the resistance increases only slightly to 13.4 milliohms. Device cycling performance was also studied with difluoromethane in the supercritical phase (fig. S4). Although the capacitance of the device is maintained, there is a substantial increase in electrolyte resistance at $+90^{\circ}\text{C}$ ($\sim 1500\%$ increase) as the salt precipitates out of the solvent because of the decreasing dielectric constant. When the temperature is lowered, the resistance decreases to nominal as the salt is solubilized back into solution and shows a slight decrease in capacitance due to accelerated cell degradation at the high temperature.

To determine whether the difluoromethane-based electrolyte offers any advantage in terms of energy density, we tested electrochemical capacitors at an elevated voltage and temperature of 3.0 V and $+65^{\circ}\text{C}$ for more than 1500 hours (Fig. 3C). The device using the acetonitrile-based electrolyte rapidly fails under these accelerated conditions, showing a substantial increase in resistance and decrease in capacitance, which agrees with previous studies of electrochemical capacitors under similar conditions (25). The difluoromethane device, however, shows little decrease in capacitance or increase in resistance under identical conditions. Similarly, a 3.0 V test was carried out at -60°C to test the low-temperature life of the device and shows nearly no change in capacitance or resistance. With a comparable capacitance already demonstrated, the increased voltage rating from 2.7 V (for typical acetonitrile devices) to 3.0 V is equivalent to a 23% increase in energy density, which offers an advantage for a range of electrochemical capacitor applications such as cold engine cranking, start-stop vehicles, and hybrid buses.

Rechargeable Li metal battery

Because of the high reduction potential of Li (-3.04 V versus normal hydrogen electrode), a thin electrically insulating, but Li-ion-conducting, solid electrolyte interphase on the Li metal instantaneously forms when in contact with many commonly used liquid solvents. Optical images of the resulting chemical products after soaking Li metal in each of the liquefied gas solvents are shown in fig. S5. The polyfluorinated solvents (difluoromethane, difluoroethane, and 1,1,1,2-tetrafluoroethane) each form a stable SEI on Li

metal, preventing further decomposition of the Li metal or solvent. Although thorough characterization of these interfaces was not done on these chemical products, the SEI is thought to be largely made up of various fluoropolymers. The monofluorinated solvents (fluoromethane, fluoroethane, and 2-fluoropropane), which are capable of solubilizing Li salts, each fully decompose Li metal into a powder form, and no stable SEI is formed. As detailed in table S2, the reaction time for the full decomposition of Li metal at room temperature in liquid fluoromethane is substantially slower than in liquid fluoroethane or 2-fluoropropane. The chemical reduction of fluoromethane by Li metal is hypothesized to follow as



Evidence for LiF and CH_3Li among the chemical products is seen in the x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) spectra shown in figs. S6 and S7, respectively, which supports this reaction scheme. Because the kinetics for Li decomposition in fluoromethane are relatively slow, and it is this solvent that had the highest electrolytic conductivity with Li salts (Fig. 2D), we explored methods to stabilize the surface of Li metal. We found that the use of carbon dioxide in additive amounts

in fluoromethane was sufficient enough to stabilize the Li surface because of the creation of a stable Li carbonate surface layer. The formation of this stable interface is shown in figs. S6 and S7, which show little evidence for LiF or CH_3Li in the SEI layer on the macroscopic level with the addition of 5 weight % (wt %) carbon dioxide. Carbon dioxide is an effective additive for use in Li-ion batteries (26), but solubility in common organic solvents is limited to ~ 0.5 wt % and strongly dependent on temperature (27). Conversely, carbon dioxide and fluoromethane are miscible solvents (28) and may enable the use of this highly effective additive in next-generation batteries.

With the addition of carbon dioxide to form a stable SEI layer on Li metal, the electrochemical stability of the fluoromethane-based liquefied gas electrolyte was determined by means of cyclic voltammetry (Fig. 4A and fig. S8). The electrolyte is limited by oxidation at 5.57 and 5.79 V versus Li at $+25^{\circ}\text{C}$ and -60°C , respectively, which is indicative of slower solvent oxidation kinetics at decreased temperatures. Carbon dioxide reduction is seen to begin at 2.1 V versus Li, which matches well with the literature (29). We observed typical Li metal plating and stripping peaks to be centered around 0 V versus Li. Although we did not observe the cathodic upper potential deposition peaks for Li and platinum (Pt) alloying because of concurrent carbon dioxide reduction, we did observe two anodic upper-deposition potential stripping peaks: a larger peak followed by a smaller peak at 0.58

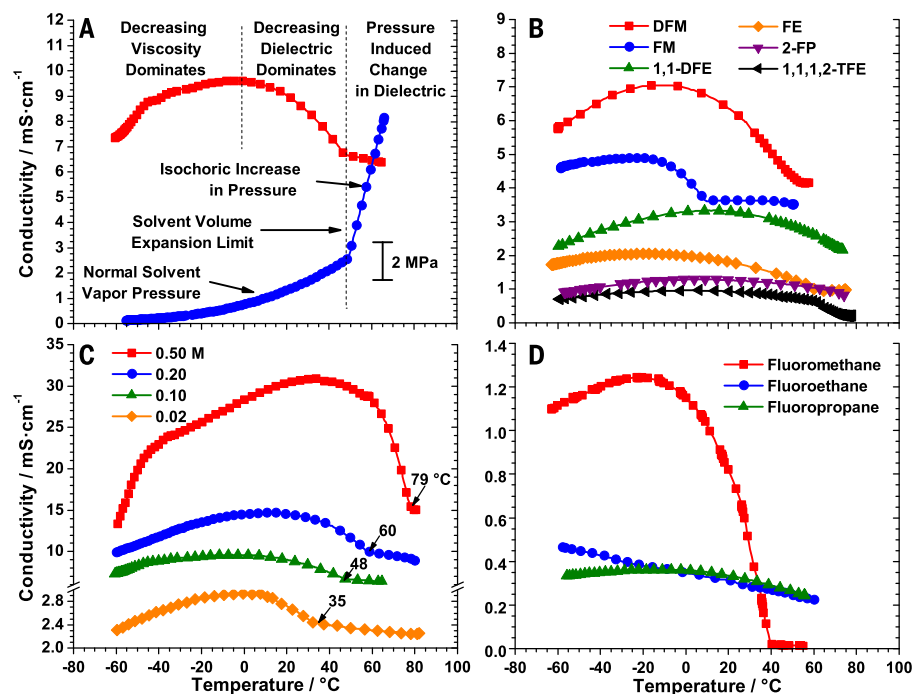


Fig. 2. Electrolytic conductivity over temperature of liquefied gas electrolytes. (A) 0.1 M TBAPF₆ in difluoromethane. (B) 0.1 M EMITFSI in various liquefied gas solvents. (C) TBAPF₆ in difluoromethane at various concentrations. (D) 0.1 M LiTFSI in various monofluorinated liquefied gas solvents.

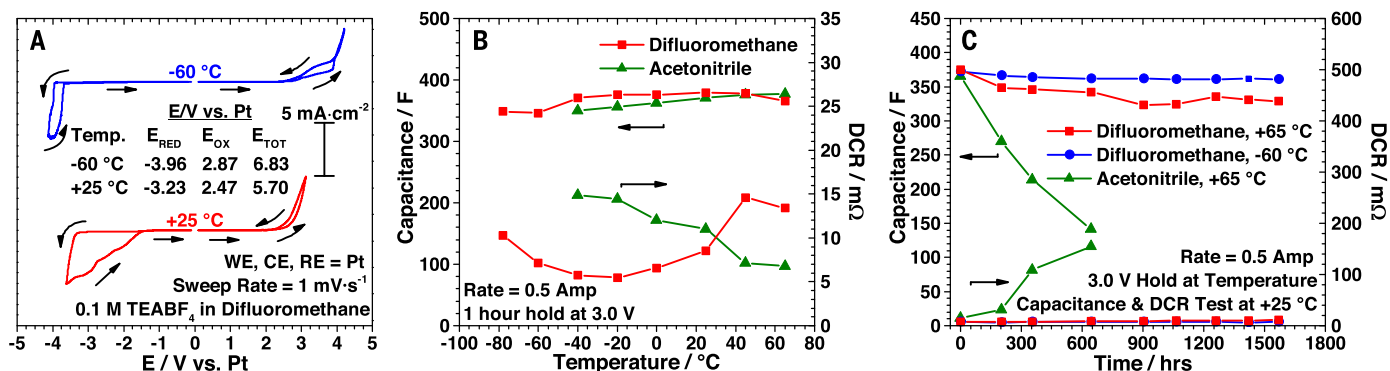


Fig. 3. Electrochemical stability of DFM and its use in electrochemical capacitors. (A) Cyclic voltammetry curves of 0.1 M TEABF₄ in difluoromethane at +25°C and -60°C. (B and C) Capacitance and resistance measurements of symmetric 350 F electrochemical capacitors using 0.5 M TEABF₄ in difluoromethane and 1 M TEABF₄ in acetonitrile (B) over temperatures from -78°C to +65°C and (C) over time with accelerated life testing at 3.0 V at -60°C and +65°C. Capacitance was measured from 2.4 to 1.2 V during a constant current discharge. Resistance was measured via the IR drop between voltage hold and constant current discharge steps.

and 1.32 V versus Li, respectively. At -60°C, we also observed a relatively high over-potential for Li nucleation, with Li deposition starting at -0.39 V versus Li.

Li metal is known to suffer from poor coulombic efficiency and severe dendrite growth in conventional electrolytes (30), but because it has the highest gravimetric capacity of all possible anodes (3863 mAh·g⁻¹), there are still numerous efforts to try to enable this anode in a rechargeable battery. Using solvents of low viscosity (31), increased pressure on the electrode (32), and a surface coverage of LiF (33) are all promising methods to improve the Li metal anode cyclability and lower the severity of dendrite formation. The exceptionally low viscosity, high vapor pressure, and LiF chemical reduction products are all properties inherent to the fluoromethane liquefied gas solvent. To explore the effectiveness of the proposed electrolyte system in enabling the Li metal anode, we measured the coulombic efficiency of Li plating and stripping on polished stainless steel electrodes. As shown in Fig. 4B, the fluoromethane-based electrolyte shows a stable and high coulombic efficiency of ~97% over 400 cycles at an aggressive 1 mA·cm⁻² plating and stripping rate, with 1 C·cm⁻² of Li being passed each cycle. For comparison, a conventional liquid electrolyte system (1 M LiPF₆ in EC:DEC 1:1) is shown to have a poor and unstable coulombic efficiency under identical cell conditions. The comparative fluoromethane and liquid electrolyte Li plating and stripping cells were stopped at 400 cycles in order to examine the stainless steel substrates with scanning electron microscopy (SEM). We found the surface morphology of the deposited Li layer from the fluoromethane-based electrolyte to be highly uniform, with micrometer-sized grain-like features and no evidence of dendrite growth (Fig. 4C). This is in contrast to the highly polymeric and dendritic-like surface observed from cycling in the liquid electrolyte (fig. S9). Further, we found the thickness of the deposited Li layer in the fluoromethane and comparative liquid electrolyte to be 60 and 460 μm thick, respectively, reflecting the far su-

perior coulombic efficiency of the novel electrolyte system. The coulombic efficiency for Li plating and stripping compares with reported values for diethyl ether: tetrahydrofuran 95:5 (98%) (34), 2-methylfuran (97%) (35), and 1,2-dioxolane (98%) (36). The high efficiencies in these systems are only seen with the use of the toxic Li hexafluoroarsenate (LiAsF₆) salt, which was reduced at the Li metal surface to form a LiF passivation layer. In the fluoromethane system, the solvent itself forms a LiF layer when reduced, which removes the need for LiAsF₆ salt. In addition, the reduction of carbon dioxide to form Li carbonate has been shown to improve the impedance and cyclability of the Li metal anode (37), which is used to stabilize the electrode in the present study. More recently, other electrolyte systems have been shown to have high Li plating and stripping efficiencies without the use of LiAsF₆, but none have demonstrated suitable oxidation stability for use with conventional 4 V cathode systems owing to the poor stability at increased potentials of these ether-based electrolytes (38). These electrolytes are mostly limited to cathode chemistries that have a low potential and limit the oxidation of these solvents; however, the ability to use a Li metal anode with a high voltage intercalation cathode would offer a substantial increase in energy density as well.

We used a Li cobalt oxide (LiCoO₂) cathode to demonstrate the high oxidation stability and compatibility of the fluoromethane-based liquefied gas electrolyte with traditional cathode materials. We used fluoromethane- and conventional liquid-based electrolyte systems for comparison in order to test this cathode under identical cell conditions. All charging and discharging of cells was done at a fixed temperature, rather than charging at a higher temperature followed by discharge at a lower temperature. The electrode performance in both electrolyte systems is shown over a number of cycles at various temperatures and C-rates (Fig. 4D), with corresponding voltage versus discharge capacity curves (Fig. 4E). At +25°C, the discharge capacity at the C/10 rate is very similar, showing ~133 mAh·g⁻¹ when using both electro-

lytes. At higher rates, the performance of the liquid electrolyte system is marginally higher than that of the fluoromethane-based electrolyte, showing a capacity retention of 87.2 and 81.2% at the 1C rate, respectively. However, at lower temperatures the high rate performance of the fluoromethane-based electrolyte is far superior. At -10°C and at the C/10 rate, the fluoromethane- and liquid-based electrolytes show a 98.3 and 86.2% discharge capacity retention relative to +25°C, respectively. At higher rates or lower temperatures, the liquid-based electrolyte fails to cycle properly because of a high cell impedance. In contrast, the cell using the fluoromethane-based electrolyte cycles fairly well at higher rates at various temperatures, most notably showing an excellent capacity retention of 60.6% at the C/10 rate at -60°C, at which traditional liquid electrolytes would generally freeze. This compares favorably with a specially developed low-temperature liquid-based electrolyte that shows a discharge capacity retention of 43.5% at the C/10 rate at -60°C by using a substantially larger-capacity full cell (39). Impedance spectra for cells at each temperature are shown in fig. S10, and fitted parameters are given in table S3. Stability of the fluoromethane-based electrolyte system is compared with the liquid electrolyte in Fig. 4F at +25°C and at a C/2 rate. Both electrolytes show very similar stability, with the fluoromethane-based electrolyte showing a 96.7% capacity retention after 100 cycles, which demonstrates the high compatibility of this electrolyte system with conventional 4 V cathodes.

The low conductivity of traditional liquid electrolytes is not a primary source of the limited low-temperature performance of Li-ion cells (40). The true origin of these limitations is likely due to charge transfer or solid electrolyte interphase impedance and is sensitive to the type of electrodes and electrolyte used (41, 42). Because identical anodes and cathodes were used in these studies, it is thought that the high performance of the fluoromethane-based electrolyte at such low temperatures is due to the substantially improved SEI layer on the electrodes. To further explore the electrode-electrolyte interphases seen in the

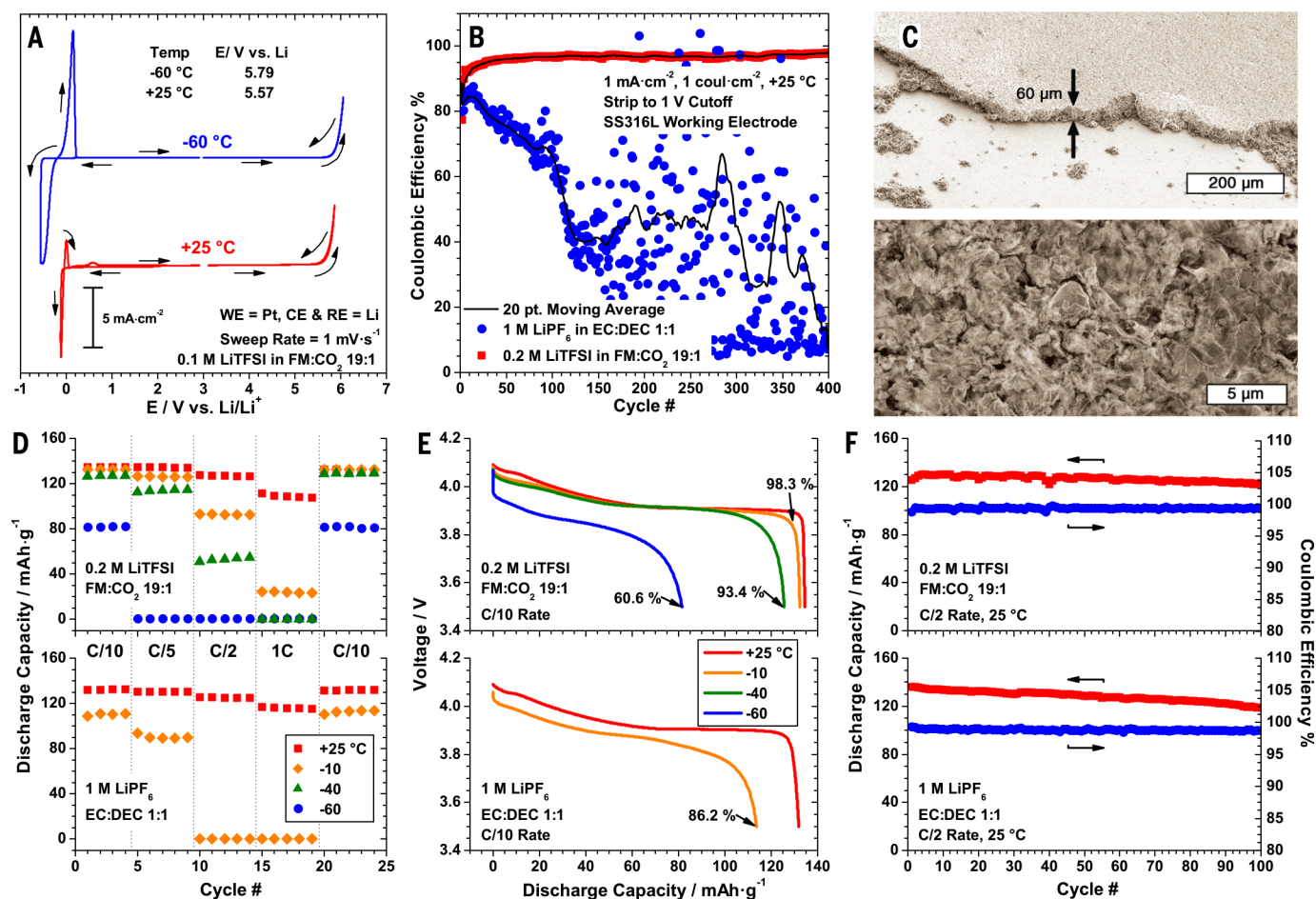


Fig. 4. Electrochemical stability of FM and its use in Li batteries.

(A) Cyclic voltammograms of 0.1 M LiTFSI in fluoromethane at +25°C and -60°C with a voltage sweep rate of 1 mV · s⁻¹, with oxidation potential limit values taken with a 200 μA · cm⁻² cutoff current. (B) Coulombic efficiency of Li plating and stripping on a SS316L working electrode over 400 cycles by using fluoromethane- and conventional liquid-based electrolytes at

+25°C. (C) SEM of the fluoromethane SS316L working electrode after the

400 cycles imaged at a 30° tilt in the lithiated state. (D) Discharge capacity over various temperatures and C-rates. (E) Voltage versus discharge capacity over various temperatures at the C/10 rate.

(F) Discharge capacity and coulombic efficiency, with cycling at the C/2 rate of a LiCo₂ electrode with a Li metal anode.

fluoromethane-based electrolyte, we conducted x-ray photoelectron spectroscopy (XPS) analysis on both the Li metal anode and LiCo₂ cathodes. As seen in Fig. 5, the surface of Li metal submerged in fluoromethane is largely composed of LiF and CH₃Li, with a minor Li₂CO₃ signal originating from impurities within the Li metal. The addition of carbon dioxide to stabilize the surface further adds a substantial Li₂CO₃ component to the SEI and lowering of the CH₃Li component—results that agree with the XRD and FTIR analyses. After cycling, the surface components show little chemical change and retain a highly ceramic-like SEI composed primarily of LiF and Li₂CO₃, in contrast to the highly polymer-like SEI formed on the surface on Li metal submerged in conventional carbonate-based electrolytes. The formation of a thin Li₂CO₃ layer via carbon dioxide reduction and the high mobility of Li ions through the grain boundaries of the highly ceramic surface are thought to both contribute to a substantially decreased impedance through the anode SEI layer. Further, the highly chemically

uniform interface as seen in the fluoromethane-based electrolyte is thought to contribute to a more uniform current distribution, which prevents dendrite formation (43).

Although the improvement on the anode is expected to improve cell performance, previous studies have shown that a substantially higher impedance occurs on the cathode, rather than on the anode, at low temperatures (44). The chemistry of the cathode-electrolyte interphase was examined via XPS (Fig. 6). Comparing the XPS spectra of LiCo₂ electrodes before cycling and after cycling, there are surprising differences. Other than evidence of a small amount of residual LiTFSI salt, there is no change in the Li 1s, C 1s, F 1s, and Co 2p spectra for the electrode cycled in the fluoromethane-based electrolyte. In contrast, the electrode cycled in the conventional liquid electrolyte shows a substantial increase of LiF on the surface of the electrode from decomposition of the PF₆⁻ anion. Whereas the O 1s shows the typical increase in polymeric-type species in agreement with other work (45), the change

occurring in the O 1s spectra of the electrode cycled in the fluoromethane-based electrolyte is not as clear. Because carbon dioxide is expected to be stable at the potentials seen at this electrode surface, and there is no other source of oxygen, the increased peak seen in the O 1s spectra is thought to be due to a change of the surface oxygen of the LiCo₂ electrode (46) and not related to the formation of an additional surface layer on the electrode. We concluded that the improved SEI on Li metal and a cathode with little or no SEI both contribute to the exceptionally high performance at low temperatures of Li batteries using these liquefied gas electrolytes.

Conclusion

Through a combination of superior physical and chemical properties, hydrofluorocarbon-based liquefied gas electrolytes are shown to be compatible for energy storage devices. The low melting points and high dielectric-fluidity factors of these liquefied gas solvents allow for exceptionally high electrolytic conductivities over a range of temperatures. High

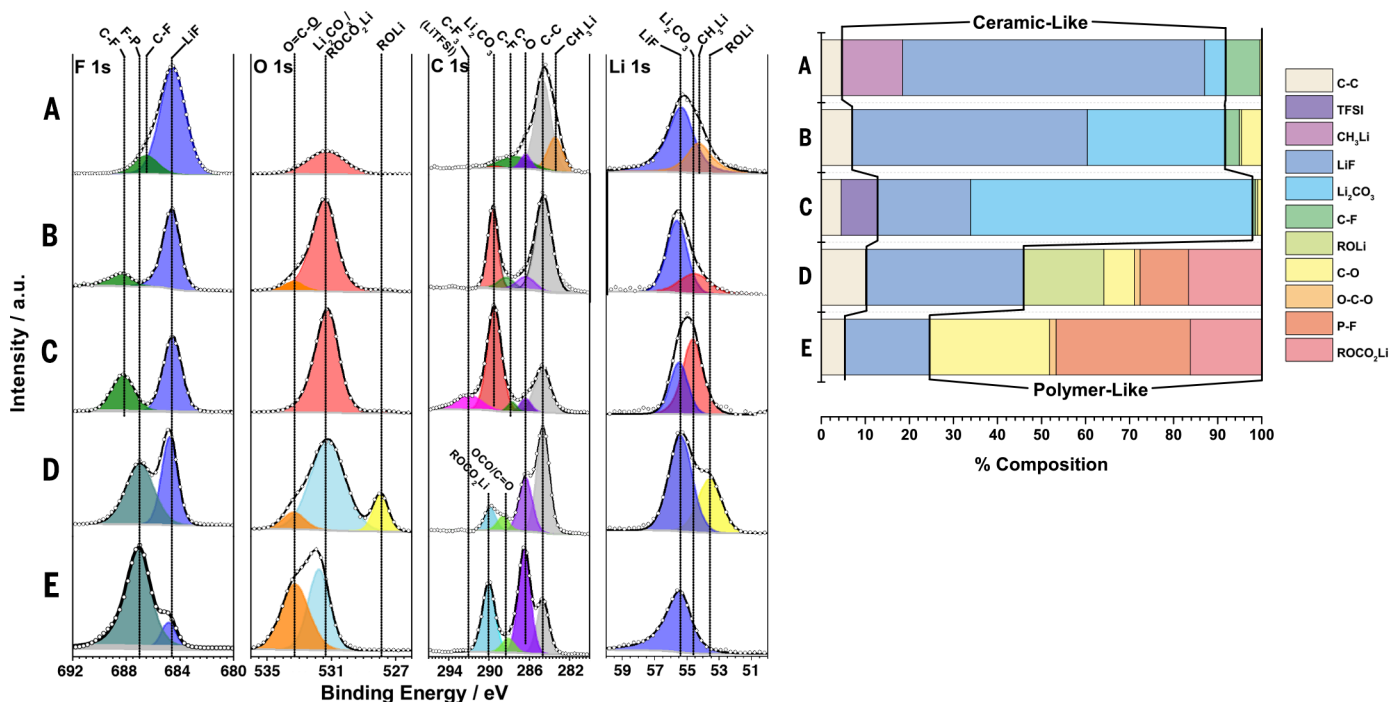


Fig. 5. XPS spectra and calculated percent composition of Li metal surface products. (A to E) Li metal after being (A) submerged in FM for three days, (B) submerged in FM:CO₂ 19:1 for three days, (C) cycled 400 times in 0.2 M LiTFSI in FM:CO₂ 19:1, (D) submerged in 1 M LiPF₆ in EC:DEC 1:1 for 3 days, and (E) cycled 400 times in 1 M LiPF₆ in EC:DEC 1:1. No washing of the Li electrode was done before XPS analysis.

performance in electrochemical capacitors and Li batteries at temperatures as low as -78°C and -60°C , respectively, has been demonstrated for potential use in aerospace and high-atmosphere applications. Comparable conductivities and performance to conventional electrolytes at moderate temperatures has also been shown, which may be applicable to more mainstream applications such as hybrid and electric vehicles. With the use of difluoromethane as an electrolyte solvent, electrochemical capacitor operation at an increased voltage under accelerated life conditions has been demonstrated, equating to a 23% increase in energy density. With the use of fluoromethane as an electrolyte solvent, a high coulombic efficiency of $\sim 97\%$ for Li metal plating and stripping with no evidence of dendritic growth as well as the compatibility with the traditional 4 V LiCoO₂ cathode offers a promising path toward developing a high-energy-density rechargeable Li metal battery.

Materials and methods

Materials

Fluoromethane (99.99%) and difluoromethane (99.99%) were obtained from Matheson Gas, fluoroethane (97%), 1,1-difluoroethane (99%), 1,1,1,2-tetrafluoroethane (99%) and 2-fluoropropane (98%) were obtained from Synquest Labs and carbon dioxide (99.9%) was obtained from Airgas. All gases were stored in high pressure refrigerant recovery tanks after use to minimize their release to atmosphere. The salts tetraethylammonium hexafluorophosphate (99.9%) and lithium bis(trifluoromethane)sulfonimide (99.9%) were purchased from BASF while all other salts (electrochemical grade) and acetonitrile (99.8%, an-

hydrous) were purchased from Sigma-Aldrich. For comparative studies, a liquid electrolyte composed of 1 M LiPF₆ in EC:DEC 1:1 by wt% was used (LP40, BASF). Dimethyl carbonate ($\geq 99\%$, anhydrous) and Nujol Oil for FTIR measurements was purchased from Sigma-Aldrich. Acetonitrile and dimethyl carbonate were dried over molecular sieves prior to use while all other materials were used as received.

For lithium battery electrodes, lithium cobalt oxide, carbon black, and lithium metal were purchased from Sigma-Aldrich, Timcal, and FMC, respectively. In lithium battery and lithium plating and stripping experiments, electrodes were electrically separated by a single porous 20 μm polypropylene separator (Celgard 2075). Commercial electrochemical capacitor jelly rolls (350 F rated) were donated from Maxwell Technologies which had no prior contact with any electrolyte solution.

Electrolytic conductivity measurements

Electrolytic conductivity measurements were performed as detailed previously (47). Briefly, four electrode electrolytic conductivity measurements were performed with a custom fabricated thin-film platinum sputtered electrode on borosilicate glass. The cell constant was calibrated from 0.1 to 100 $\text{mS}\cdot\text{cm}^{-1}$ with a measurement accuracy of $\pm 6\%$. The thin film electrode ensured there would be no geometric change, and hence cell-constant change, under the increased pressures resulting from the studied electrolytes.

Electrochemical capacitors

For electrochemical capacitor testing, jelly rolls were dried overnight under vacuum at $+180^{\circ}\text{C}$.

Custom cells were designed to make a four wire measurements to the jelly roll in order to obtain accurate resistance measurements. All metal contacts were made of aluminum to avoid corrosion issues during cell test. Cell assembly was all done under argon atmosphere.

Resistance (DCR) measurements were calculated from the instantaneous iR drop (captured on a high resolution potentiostat) resulting from a 0.5 Amp discharge current after holding at 3 V for 1 hour. Capacitance was measured as

$$\text{Capacitance} = I \cdot (t_2 - t_1) / (V_2 - V_1)$$

where I , V_2 and V_1 were set at -0.5 Amp, 2.4 and 1.2 V, respectively.

Rechargeable lithium metal battery

For rechargeable lithium metal battery testing, electrode slurries composed of LiCoO₂: carbon black: PVDF binder at a 8:1:1 ratio by weight were mixed with an appropriate amount of N-Methyl-2-pyrrolidone (NMP) solvent and doctor bladed onto 25 μm thick stainless steel 316L foil. The thickness of the coated active electrode after cold calendaring was *ca.* 40 μm thick. Active mass loading was *ca.* 0.9 $\text{mAh}\cdot\text{cm}^{-2}$ or 6.6 $\text{mg}\cdot\text{cm}^{-2}$ (assuming a theoretical capacity of 137 $\text{mAh}\cdot\text{g}^{-1}$ when cycled between 3.5 and 4.1 V). Electrodes of 0.31 cm^2 were used for cell testing. Lithium metal was purchased from FMC and was scrapped clean with a glass slide and rolled with a polyethylene rod to a mirror finish prior to all experiments. Electrodes were electrically separated by a single porous 20 μm polypropylene separator and placed inside a custom fabricated

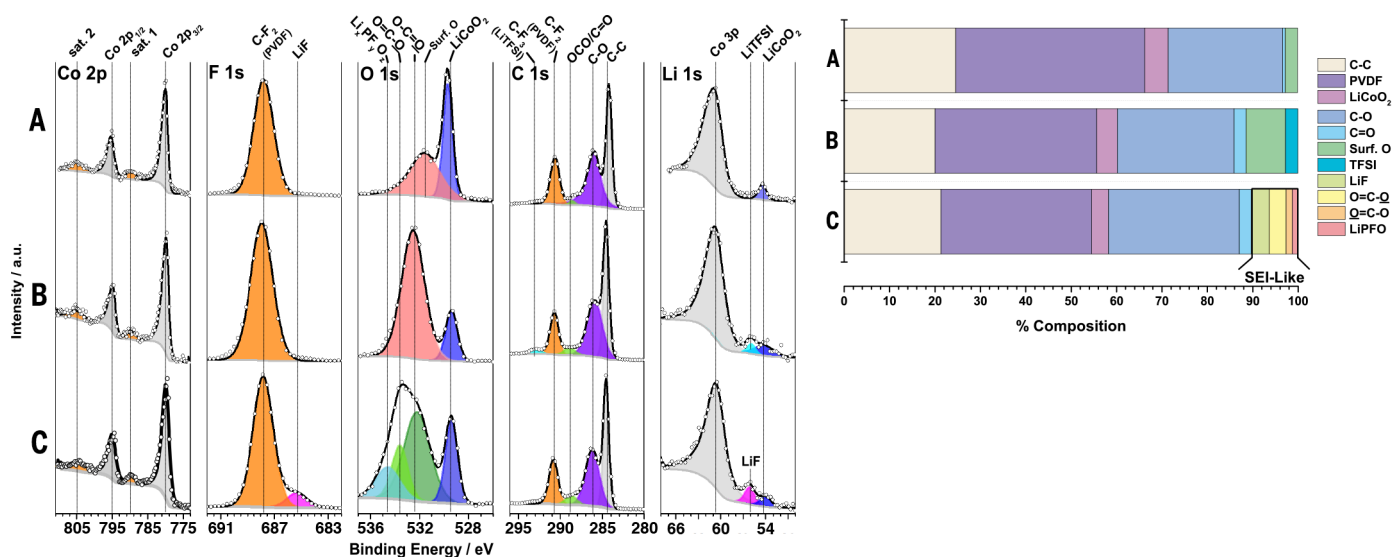


Fig. 6. XPS spectra and calculated percent composition of a LiCoO_2 electrode. (A to C) Electrodes (A) before cycling and after cycling five times from 3.5 to 4.1 V versus Li with (B) 0.2 M LiTFSI in FM:CO₂ 19:1, and (C) 1 M LiPF₆ in EC:DEC 1:1. XPS spectra in (B) and (C) were taken in the lithiated state at 3.5 V versus Li after washing with dimethyl carbonate.

coin cell constructed of high density polyethylene equipped with stainless steel 316L current collectors for both electrodes. All cell assembly was done under an argon atmosphere.

For lithium plating and stripping coulombic efficiency tests, cells were similarly prepared except the LiCoO_2 electrode was not used and lithium was directly plated to the stainless steel 316L current collectors, used here as working electrodes, which were polished to a mirror finish. In all tests, all wetted metal components were stainless steel 316 to avoid corrosion issues.

Electrolyte addition

To form the liquefied gas electrolyte solution, a weighed amount of salt was first pre-loaded into high pressure stainless steel cells along with the capacitor or battery device and sealed under argon atmosphere. The cells were then cooled to a low temperature (*ca.* -60°C) and a controlled amount of solvent was allowed to evaporate from the source and condense into the cell using a mass flow controller (MKS) through a tube connected to the cell, which was then sealed shut with an attached valve. For comparative studies, conventional liquid electrolytes were added under argon atmosphere prior to cell sealing. Cells for comparative study using liquid electrolytes were otherwise mechanically identical to the liquefied gas electrolyte based cells and electrodes were similarly submerged under electrolyte solution.

Thermal and electrochemical characterization

For thermal testing, cells were allowed to thermally equilibrate inside a temperature chamber (Espec) before beginning test. Dry ice was used to cool the cells for tests conducted at -78°C. Temperature measurements were made from a Type K thermocouple with an uncertainty of $\pm 2^\circ\text{C}$ and

pressure measurements were recorded from a digital pressure transducer (Omega Engineering) with an uncertainty of $\pm 2\%$ of the measured pressure. Temperature and pressure measurements were recorded with a digital data acquisition system (Agilent).

All electrochemical tests were conducted inside high pressure stainless steel cells equipped with electrical feedthroughs which were electrically connected to test electrodes. Cyclic voltammetry experiments were performed with a sweep rate of $1 \text{ mV}\cdot\text{s}^{-1}$. Non-lithium-based electrolytes used sputtered platinum counter and reference electrodes. Lithium-based electrolytes used lithium metal counter and reference electrodes. All electrolytes used sputtered platinum working electrodes with an area of 1 mm^2 (exposed area defined by a *ca.* 250 nm thick silicon dioxide passivation layer) on borosilicate glass. Separate platinum working electrodes were used for anodic and cathodic potential regions as well as for each temperature to avoid effects from a previous polarization of the working electrode. Potential windows were calculated at the point where current increased beyond $200 \mu\text{A}\cdot\text{cm}^{-2}$. Battery electrochemical impedance measurements were conducted with a sinusoidal probe voltage of 5 mV and spectra were fitted with ZView software. All electrochemical capacitor cycling, cyclic voltammetry and impedance measurements were conducted with an SP-200 potentiostat (Bio-Logic).

Lithium battery cell cycling was performed with a battery cycler (Arbin). For LiCoO_2 cell tests, cycling consisted of a 100% depth of discharge from 3.5 to 4.1 V for all measurements. For lithium plating and stripping experiments, a single cycle consisted of plating lithium metal to the polished stainless steel 316L working electrode at a current density of $1 \text{ mA}\cdot\text{cm}^{-2}$ with a total charge transfer of $1 \text{ coul}\cdot\text{cm}^{-2}$, followed by lithium strip-

ping at $1 \text{ mA}\cdot\text{cm}^{-2}$ till the working electrode potential rose above 1 V vs. Li/Li⁺, at which point the current was immediately reversed and the following cycle commenced. The coulombic efficiency was simply calculated as

$$\text{Efficiency \%} = 100 \cdot (Q_{\text{strip}}) \cdot (Q_{\text{plate}})^{-1}$$

where Q_{strip} is the amount of charge passed during the lithium stripping cycle and Q_{plate} is the amount of charge plated ($1 \text{ coul}\cdot\text{cm}^{-2}$) each cycle.

Materials characterization

Powder x-ray diffractions (XRD) of samples were collected on a either a Bruker D8 or Bruker D2 Phaser using Cu $K\alpha$ radiation. Continuous scanning of a detector covering angles from 10.0° to 80.0° with a scan rate of *ca.* $0.02^\circ \text{ s}^{-1}$ and wavelength of $\lambda = 0.154 \text{ nm}$. Air sensitive samples were sealed under argon atmosphere in polyethylene heat sealed bags and their backgrounds are included in the XRD background spectra.

Fourier transform infrared (FTIR) measurements were conducted with a liquid nitrogen cooled Nicolet 6700 Analytical MCT FT-IR Spectrometer using an Attenuated Total Reflectance (ATR) accessory (single bounce, Diamond/ZnSe crystal). For lithium metal measurements, samples were submerged into Nujol Mineral oil under an argon atmosphere. The samples were then transferred in a sealed vial then quickly clamped down with a polyethylene plastic backing onto the ATR crystal. This allowed Nujol oil to spread around the sample, protecting it from the atmosphere. Measurements over several minutes were made to ensure there was no change in FTIR spectra due to atmospheric reaction.

Scanning electron microscopy images were taken on a FEI XL30 SFEG equipped with Ultra High Resolution (UHR) scanning mode at a beam energy of 5 keV. The lithium metal samples imaged

were quickly transferred from a vial sealed under argon atmosphere to the SEM chamber to minimize atmospheric exposure. To measure film thickness, a sharp blade was used to cut down the center of the film and the cross section was viewed under SEM at a 30° angle.

X-ray photoelectron spectroscopy measurements were carried out with a AXIS Supra by Kratos Analytical Inc. using monochromatized Al K α radiation ($h\nu = 1486.7$ eV) as X-ray source with a base pressure of 10^{-8} Pa. To avoid moisture or air exposure, the XPS spectrometer was directly connected to argon atmosphere filled glove box in which samples were prepared for analysis. The analyzed area of all XPS spectra was $300 \times 700 \mu\text{m}^2$. XPS was performed with a pass energy of 15 keV and high resolution scans with a step size of 0.05 eV were collected after a survey scan with a step size of 1.0 eV, for lithium 1s, carbon 1s, oxygen 1s, nitrogen 1s, fluorine 1s, and cobalt 2p regions. All of the obtained XPS spectra were analyzed by CasaXPS software and calibrated with a hydrocarbon C 1s signal at 284.6 eV. Core peaks were performed using nonlinear Shirley-type background. The curves were smoothed by a weighted least-squares algorithm and fitted by line shaped composed of 70% Gaussian and 30% Lorentzian. Lithium metal samples were not washed, but in the case of liquid electrolyte, were allowed to dry to remove the majority of the electrolyte from the surface. Cycled LiCoO $_2$ electrodes were discharged to 3.5 V vs. Li before XPS analysis and were washed with dimethyl carbonate to remove residual salt. Samples were prepped under argon atmosphere.

Numerical calculations

Ionization potentials and electron affinities of solvents were calculated via ab initio molecular orbital theory using Gaussian 09W on an isolated molecule in the gas phase. Solvent structures were first geometrically optimized in the ground state at the B3LYP/6-31+g(d,p) level of theory. The ionization potential and electron affinity were calculated from the difference in the electronic energy between the ground state and radical solvent molecules with identical ground state geometry through a vertical electronic transition (Franck-Condon principle). Electrostatic maps of the solvents were visualized via GaussView.

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SUPPLEMENTARY MATERIALS

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Liquefied gas electrolytes for electrochemical energy storage devices

Cyrus S. Rustomji, Yangyuchen Yang, Tae Kyoung Kim, Jimmy Mac, Young Jin Kim, Elizabeth Caldwell, Hyeseung Chung and Y. Shirley Meng

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Separating charges is a gas

Solid and liquid electrolytes allow for charges or ions to move while keeping anodes and cathodes separate. Separation prevents short circuits from occurring in energy storage devices. Rustomji *et al.* show that separation can also be achieved by using fluorinated hydrocarbons that are liquefied under pressure. The electrolytes show excellent stability in both batteries and capacitors, particularly at low temperatures.

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Supplementary Material for

Liquefied gas electrolytes for electrochemical energy storage devices

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Supplementary Text
Figs. S1 to S10
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XPS Analysis: XPS spectra for lithium foil submerged in fluoromethane for three days is shown in **Figure 5A**. Two peaks at 54.1 and 55.5 eV in the Li 1s spectrum correspond to CH_3Li and LiF respectively (56, 57), which is in agreement with the XRD and FTIR data shown in **Figures S6** and **Figure S7**, respectively. In the C 1s spectrum, the peak at 283.4 eV attributed to CH_3Li (57) and the wide peak C-F peak at 288 eV is thought to originate possibly from reduction of fluoromethane via proton abstraction, leaving the C-F bond intact. The small C-O peak at 286.3 eV and the peak at 531.3 eV in the O 1s spectra must result from the oxygen impurities in both the lithium metal and fluoromethane solvent since no other source of oxygen is present. The LiF (684.6 eV) and C-F (686.7 eV) peaks in F 1s spectra agree with peaks in Li 1s and C 1s spectra. The resulting analysis supports the theory that fluoromethane is decomposed on the lithium metal surface, in which LiF and CH_3Li are main products. However, the layer formed on lithium surface is not compact or electrically insulating enough to prevent the further reduction of the solvent, which results in complete decomposition of the lithium metal.

Carbon dioxide is reduced at the lithium surface to form a thin and electrically insulating Li_2CO_3 layer, as evidenced in both the Li 1s spectrum (54.5 eV) and C 1s spectrum (289.5 eV). The LiF peaks at 55.5 and 684.7 eV in the Li 1s and F 1s spectra, respectively, indicate fluoromethane is still reduced at the lithium surface even with addition of CO_2 . Methyl lithium, however, is absent in the bulk of the SEI since CO_2 is thought to react with CH_3Li to form $\text{CH}_3\text{CO}_2\text{Li}$ (58) and may still further decompose into other compounds, which may additionally contribute to the C-O peaks at 286.3 and 533.4 eV. The formed SEI composed of LiF and Li_2CO_3 acts as a suitable passivation layer to prevent further chemical reduction of the electrolyte system.

The surface of the lithium metal counter electrode used in plating and stripping experiments was analyzed with XPS after 400 cycles with data shown in **Figure 5C**. All peaks seen in the non-cycled lithium metal surface in Figure 5B are also present in the cycled lithium metal surface except the C-O peak at 533.4 eV, which is possibly due to a lower formation rate of CH_3Li decomposition products during cycling. An additional peak is visible at 292.0 eV due to the C-F₃ bonding in the C 1s spectrum, which corresponds to trace LiTFSI salt in SEI surface (59) or possibly CHF_3 from reduced TFSI⁻ the ion (60). Further comparing cycled and non-cycled spectra, there is an apparent increase in Li_2CO_3 relative to other components and makes up the majority of the SEI. This indicates the reduction of carbon dioxide, even at 5 wt%, is greatly preferred to the reduction of fluoromethane during electrode cycling and is likely a primary reason for the high and stable plating and stripping efficiency seen in these novel electrolytes.

Figure 5D and **Figure 5E** present typical XPS spectra for lithium metal which has been submerged and cycled (400 cycles) in a conventional liquid electrolyte system (1 M LiPF_6 in EC:DEC 1:1), respectively. Lithium metal electrodes treated with numerous conventional liquid electrolytes and salts has been comprehensively investigated by many groups, particularly D. Aurbach's group (61). Previous studies revealed that both EC and DEC are reduced on the lithium surface to ROCO_2Li species and small amount of ROLi. Further, LiF will be formed by the decomposition of LiPF_6 (61). Our XPS results agree well with these results. In C 1s spectrum, the peaks at 284.6, 286.3, 288.2 and 289.9 eV corresponds to hydrocarbon, C-O, O-C-O and $-\text{OCO}_2\text{Li}$ species, respectively. For LiF, both 55.5 eV and 684.7 eV peaks appear in the spectrum. The peaks at 53.5 and 527.8 eV also reflect the formation of ROLi which may be a decomposition product of a larger RORO_2Li type polymer (61). The broad peak at 687.0 eV is assigned to F-P from LiPF_6 decomposition (62). After 400 cycles, ROLi peaks at 53.5 and 527.8 eV disappeared and intensity of peaks associated to ROCO_2Li increased. The peak at 533.3 eV increases after cycling, corresponding to formation of additional C-O bond species in the SEI layer. Further, the proportion of

F-P species also increases, which suggest that both electrolyte and LiPF_6 salt continuously decompose at the interface during cycling.

To explore the SEI layer formed at higher potentials, XPS was also performed on LiCoO_2 electrodes before and after five cycles at the C/10 rate at +25 °C (discharged to 3.5 V vs. Li prior to analysis). **Figure 6A** shows a XPS spectrum of a LiCoO_2 electrode prior to cycling. The Co 2p shows a clearly distinguished profile with the 2p_{3/2} and 2p_{1/2} components at 780.3 and 795.1 eV. The satellite peaks are located 10 eV higher in binding energy than the main peaks, as expected. The peaks at 54.3 and 529.6 eV in the Li 1s and O 1s spectra, respectively, correspond to bulk LiCoO_2 . The broad peak at 531.6 eV of the O 1s spectrum results from both organic species and surface defects of LiCoO_2 , which have a deficient coordination (63, 64). The peaks located at 290.7 and 688.0 eV in Li 1s and F 1s spectra, respectively, are attributed to the C-F₂ bond present in the PVDF binder. These peak positions correspond well with previously reported data (65, 66).

After five cycles in the liquefied gas electrolyte (0.2 M LiTFSI in FM:CO₂ 19:1), there was little change from the pre-cycled spectrum shown in **Figure 6B**. There are small peaks in the Li 1s, C 1s and O 1s spectra corresponding to residual salt which was not removed through washing with dimethyl carbonate. Since carbon dioxide is expected to be stable at the potentials seen at this electrode surface and there is no other source of oxygen, the increased peak seen in the O 1s spectra is thought to be due to a change of the surface oxygen of the LiCoO_2 electrode (46, 60) and not related to the formation of an additional surface layer on the electrode. There were no other major changes seen in the XPS spectra, indicating very little, if any, SEI layer is formed on the surface of the cathode in the fluoromethane based electrolyte system.

In contrast to the fluoromethane based electrolyte, after five cycles in a conventional liquid electrolyte (1 M LiPF_6 in EC:DEC 1:1), there is substantial change in the F 1s and O 1s XPS spectra, shown in **Figure 6C**. The new peak at 685.2 eV is characteristic of LiF, which is also evident with the appearance of the LiF characteristic peak at 56.3 eV in Li 1s spectrum. The LiF component is commonly cited to be a decomposition product of the PF_6^- anion at the cathode surface (45). Further, there are numerous peaks which appear in the O 1s spectrum, including a peak at 534.7 eV which is assigned to oxygen atoms in fluorophosphate intermediates, namely, $\text{Li}_x\text{PF}_y\text{O}_z$. The decomposition of the electrolyte at the surface of the LiCoO_2 cathode and resulting SEI greatly contributes to the increased impedance of the cathode, particularly at low temperatures (63).

Safety and Environmental Aspects: Hydrofluorocarbons are commonly used in the refrigerant and microelectronics industries. As the use of these solvents in electrolytes for energy storage devices is not common, it is important to note the associated safety and environmental concerns. With high volatility, little solubility in water and their relatively chemically stable nature, the hydrofluorocarbon solvents themselves are generally non-toxic. However, their combustion or decomposition products may include hydrogen fluoride which may be highly toxic to humans. Throughout the scope of this work, caution was taken and there was never an instance of fire combustion. However, there was a single instance where hydrogen fluoride was noted to be evolved which was from the chemical decomposition of liquid 2-fluoropropane at a relatively high temperature (indicated by a damaged glass conductivity measurement electrode inside solution), after which the use of this solvent was ceased. The hydrofluorocarbon solvents studied range from non-flammable to highly flammable and with low to high global warming potential. In general, highly/lower fluorinated compounds will show lower/higher flammability and higher/lower global warming potential. The global warming potentials of the hydrofluorocarbons studied are tabulated in **Table S4**. Throughout the scope of this work, solvents were

stored in recovery tanks after their use to limit their release to the atmosphere. If these solvents were used on a large scale in energy storage devices, a properly hermetically sealed cell should prevent their release to the atmosphere and proper end-of-life recycling should be incorporated. A more thorough review of safety and environmental concerns relating to hydrofluorocarbons is given elsewhere (67). Throughout the scope of this work, high pressure stainless steel cells and tubing was used with substantially higher rated pressures than the highest vapor pressures of the solvents. While the vapor pressures of the solvents themselves are moderate, considerable pressure may be observed at higher temperatures if the thermal expansion of the solvents is restricted and caution should be taken in these scenarios.

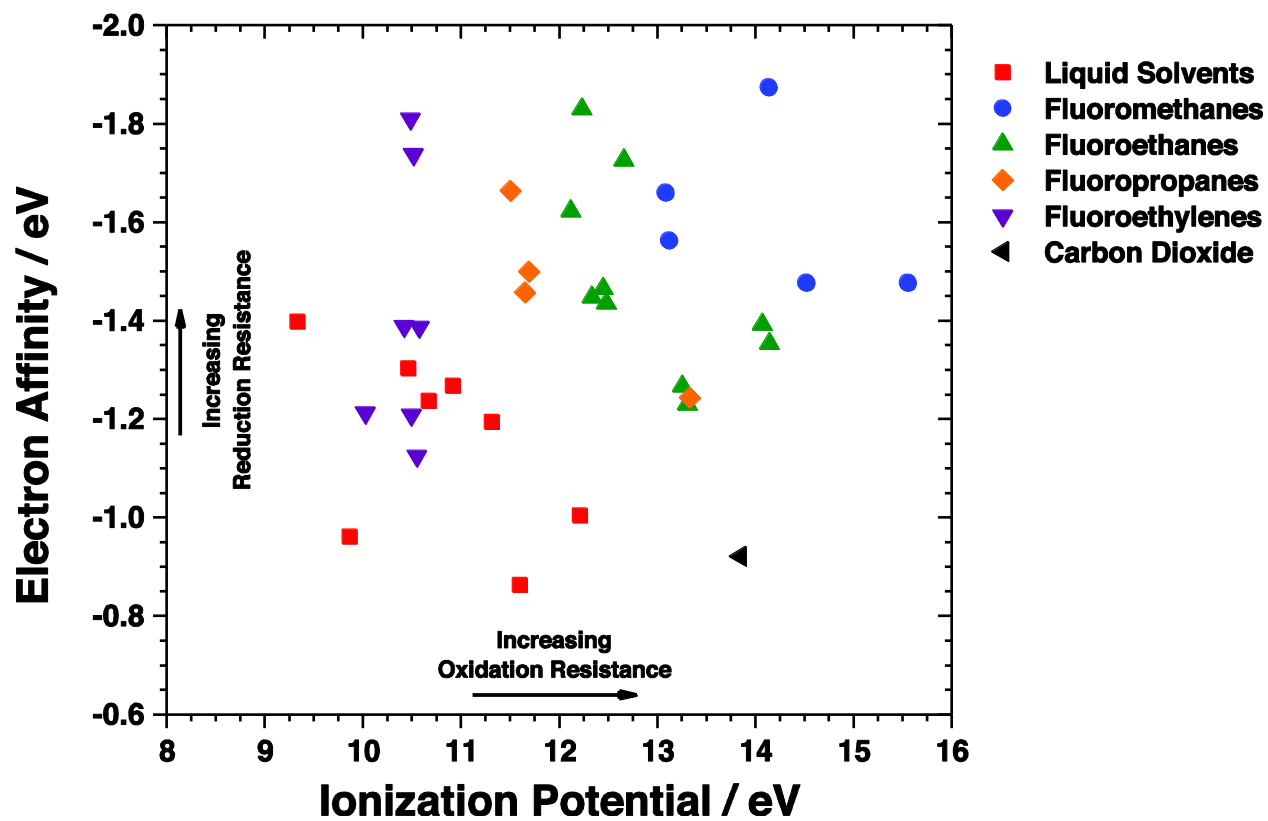


Figure S1. Ionization potential and electron affinity of liquefied gas solvents. Values for the ionization potential and electron affinity of various groups of solvents as calculated by DFT and tabulated in Table S1.

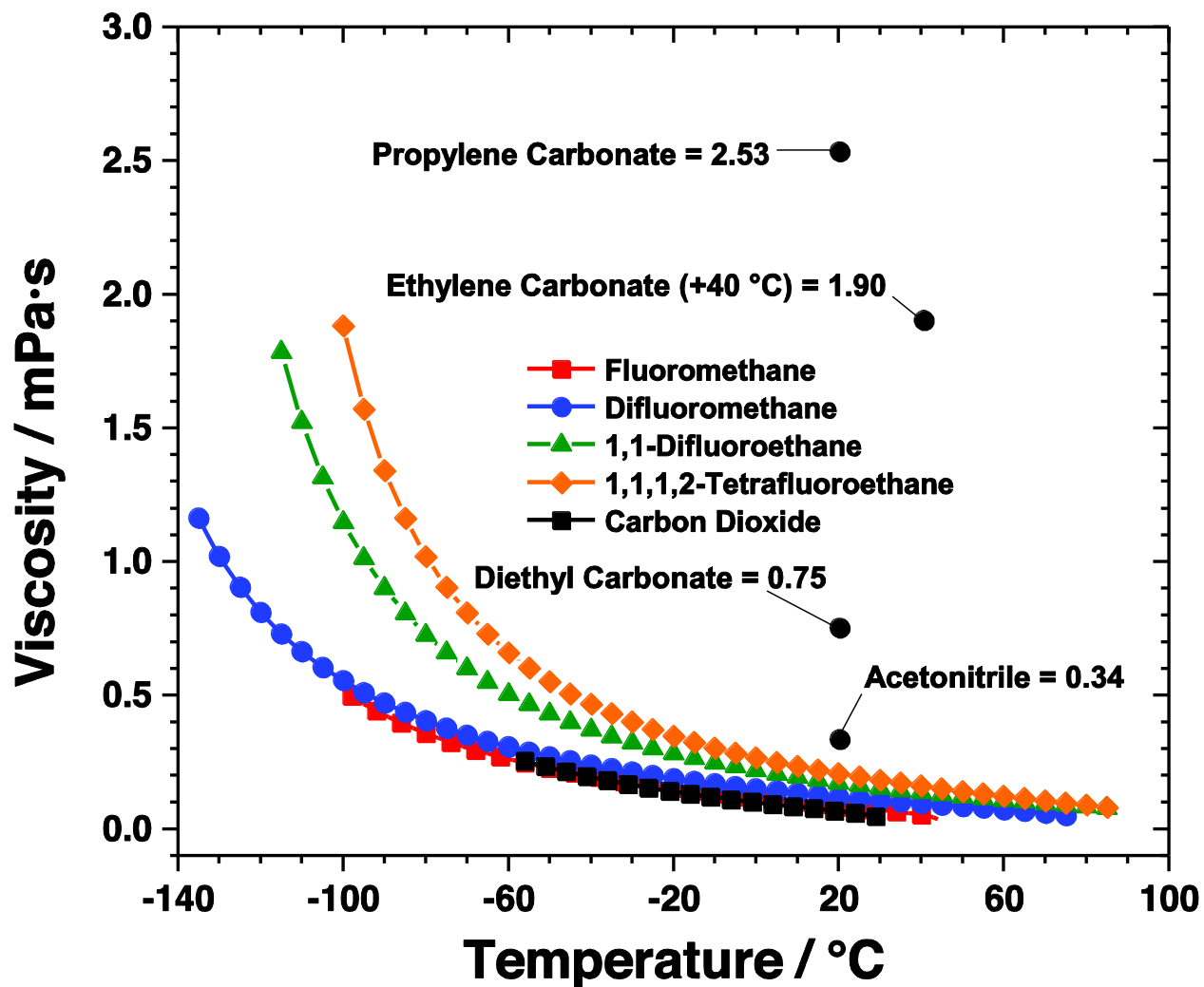


Figure S2. Viscosity of liquefied gas solvents. Viscosity as a function of temperature for select liquefied gas solvents and comparative conventional liquid solvents (16).

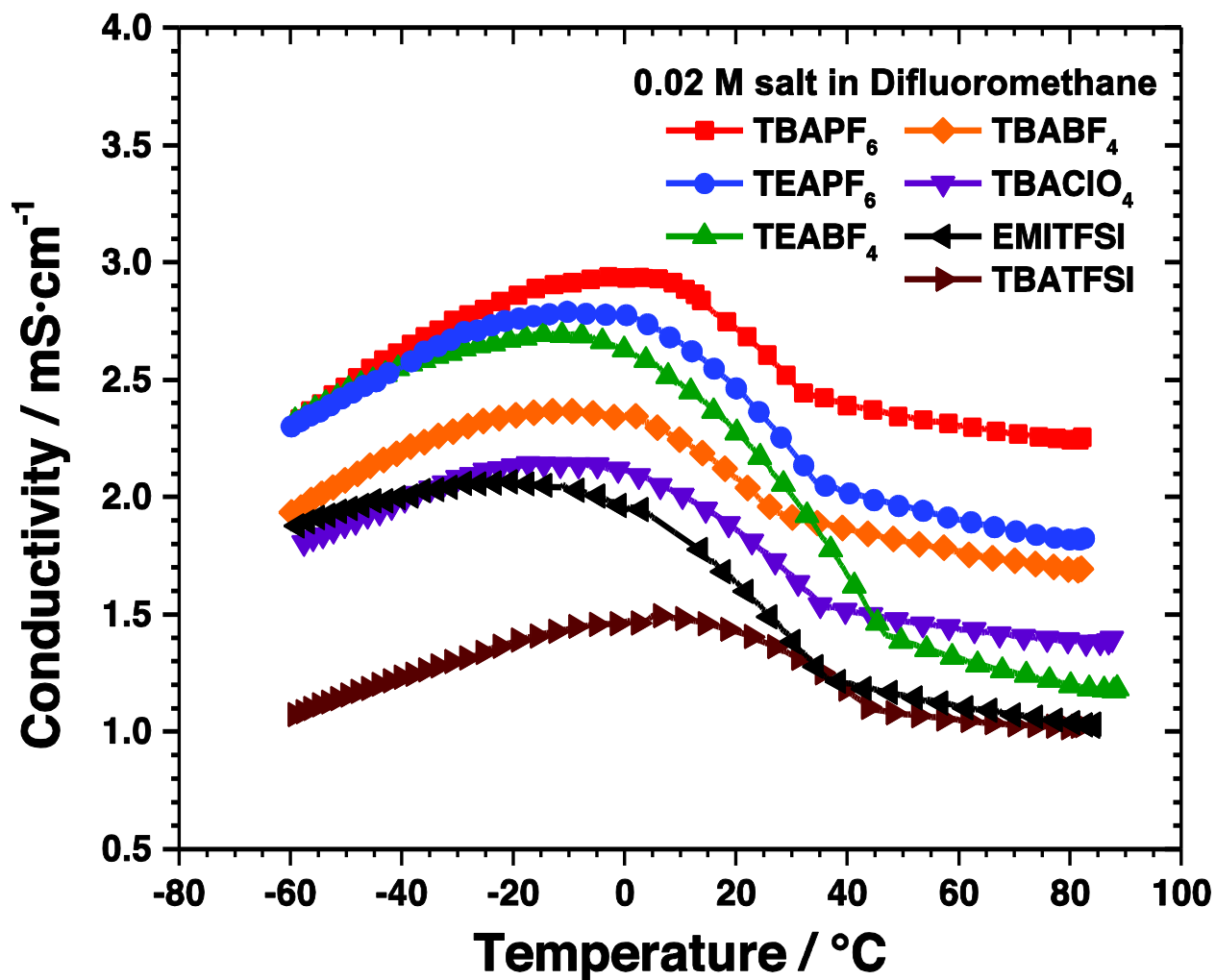


Figure S3. Electrolytic conductivity of difluoromethane based electrolytes. Electrolytic conductivity as a function of temperature for various salts in difluoromethane.

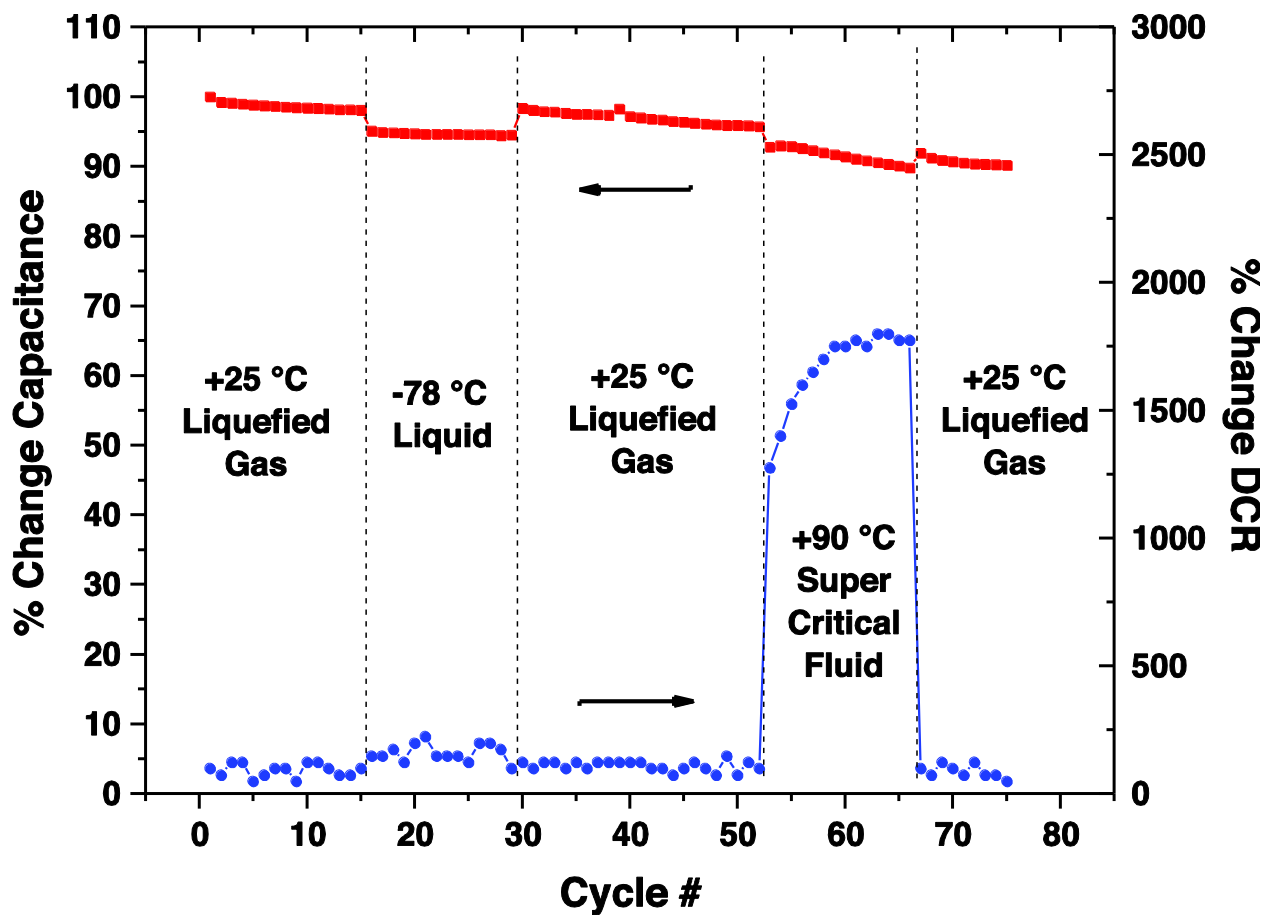


Figure S4. Electrochemical capacitor performance. Percent change in capacitance and resistance of an electrochemical capacitor over many cycles at various temperatures.



Figure S5. Optical images of lithium metal after submersion in liquefied gas solvents. Reaction products as a result of submerging lithium metal in six different liquefied gas solvents, with bare lithium metal (left most image) for comparison. All samples were submerged in solvent till all chemical reaction activity was seen to cease, times which are tabulated in **Table S2**.

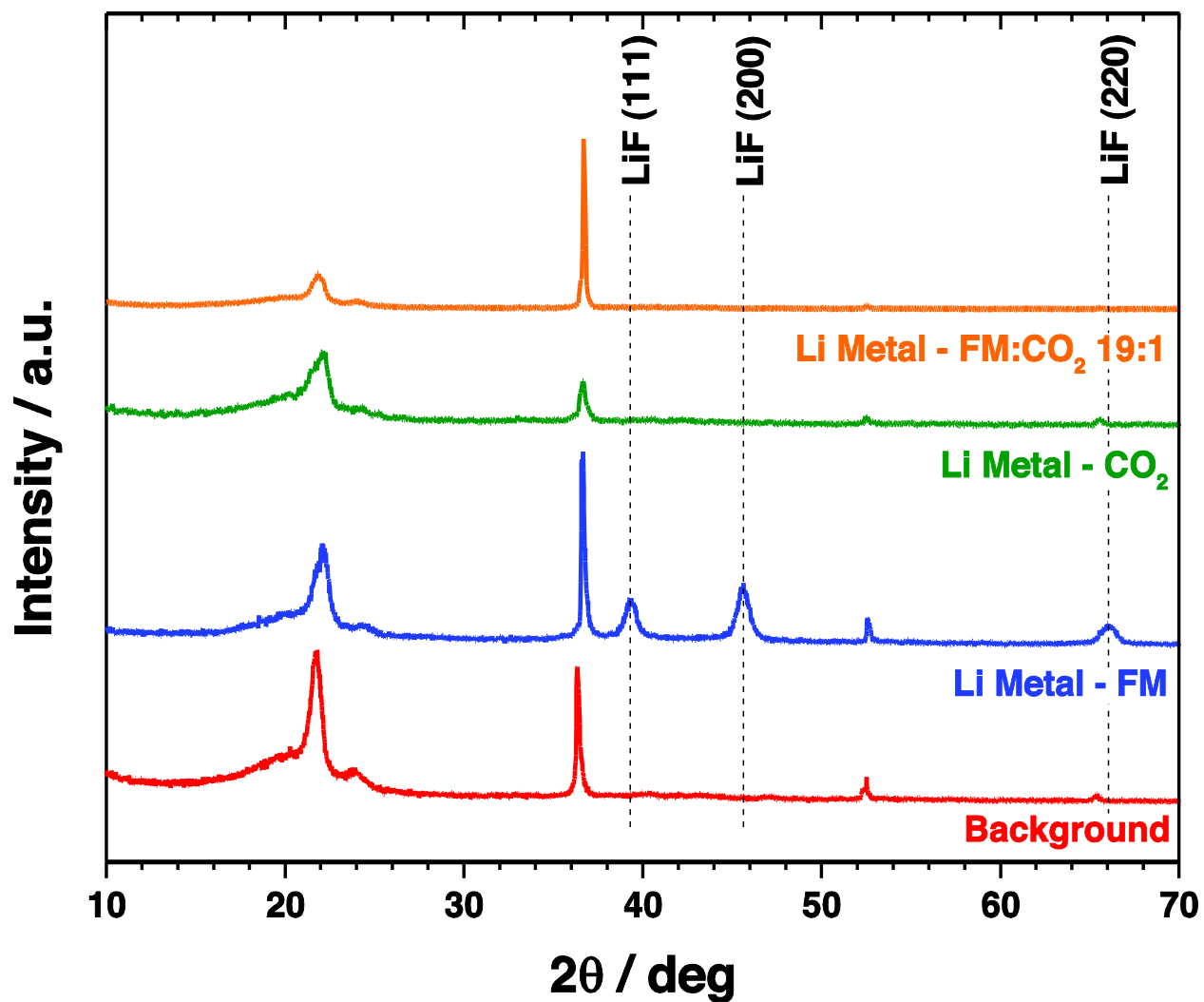


Figure S6. XRD spectra of lithium metal after submersion in liquefied gas solvents. Spectra of lithium metal submerged in fluoromethane, carbon dioxide and a mixture of FM:CO₂ 19:1 after five days. Solvents were all in the liquid state at +25 °C during lithium submersion.

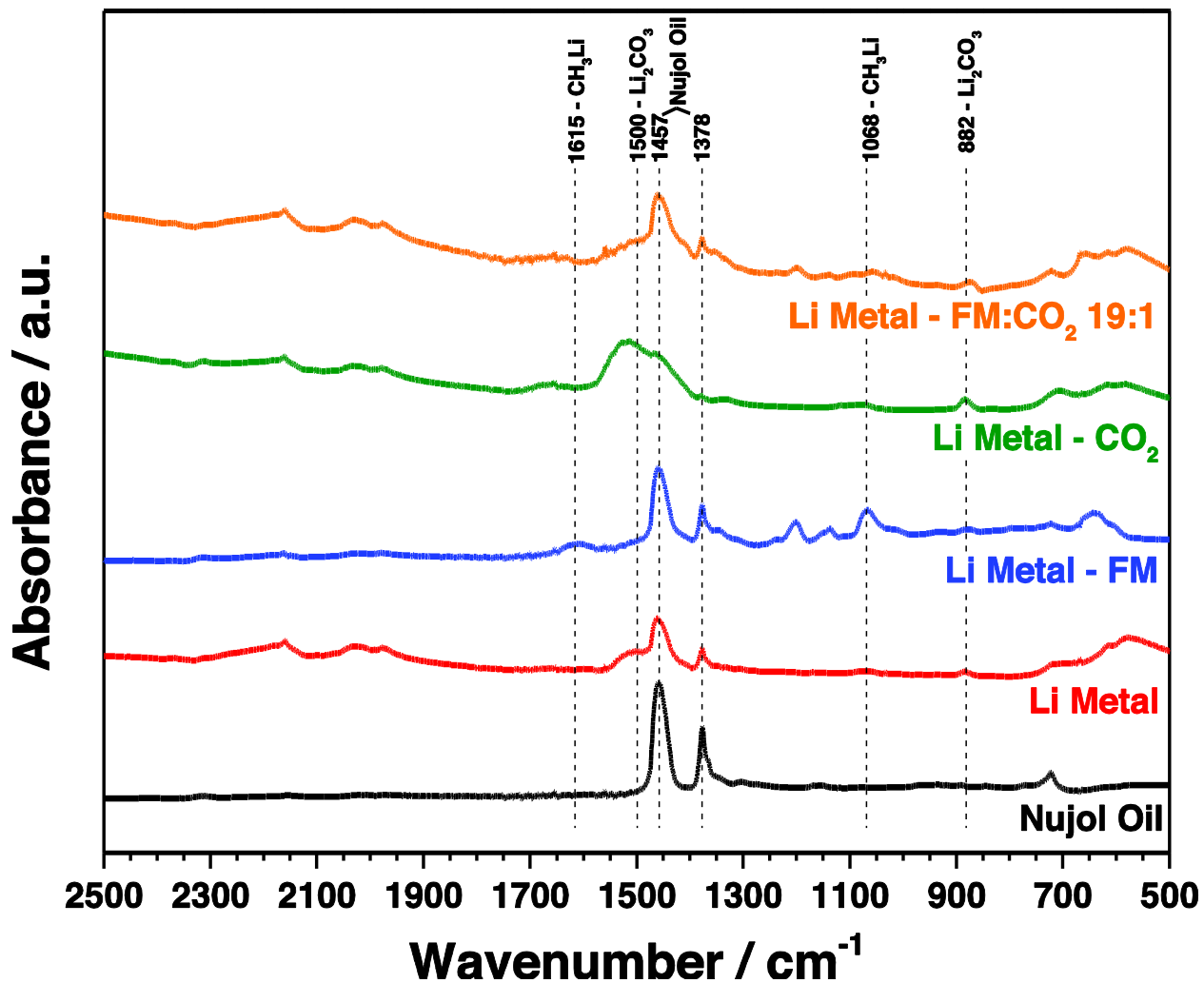


Figure S7. FTIR spectra of lithium metal after submersion in liquefied gas solvents. Spectra of fluoromethane, carbon dioxide and a mixture of FM:CO₂ 19:1 after five days. Solvents were all in the liquid state at 25 °C during lithium submersion. Methyl lithium FTIR peaks identified from previous work (68).

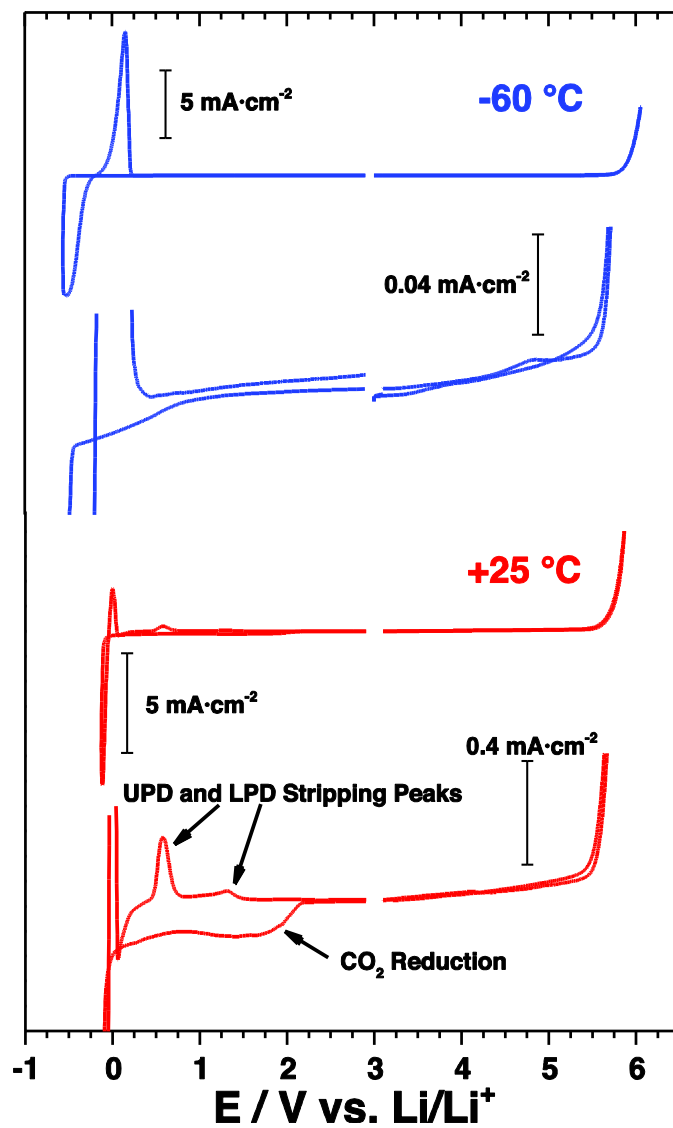


Figure S8. Electrochemical stability of fluoromethane. Cyclic voltammograms of 0.2 M LiTFSI in FM:CO₂ 19:1. WE = Pt, CE & RE = Li metal, sweep rate = 1 mV·sec⁻¹.

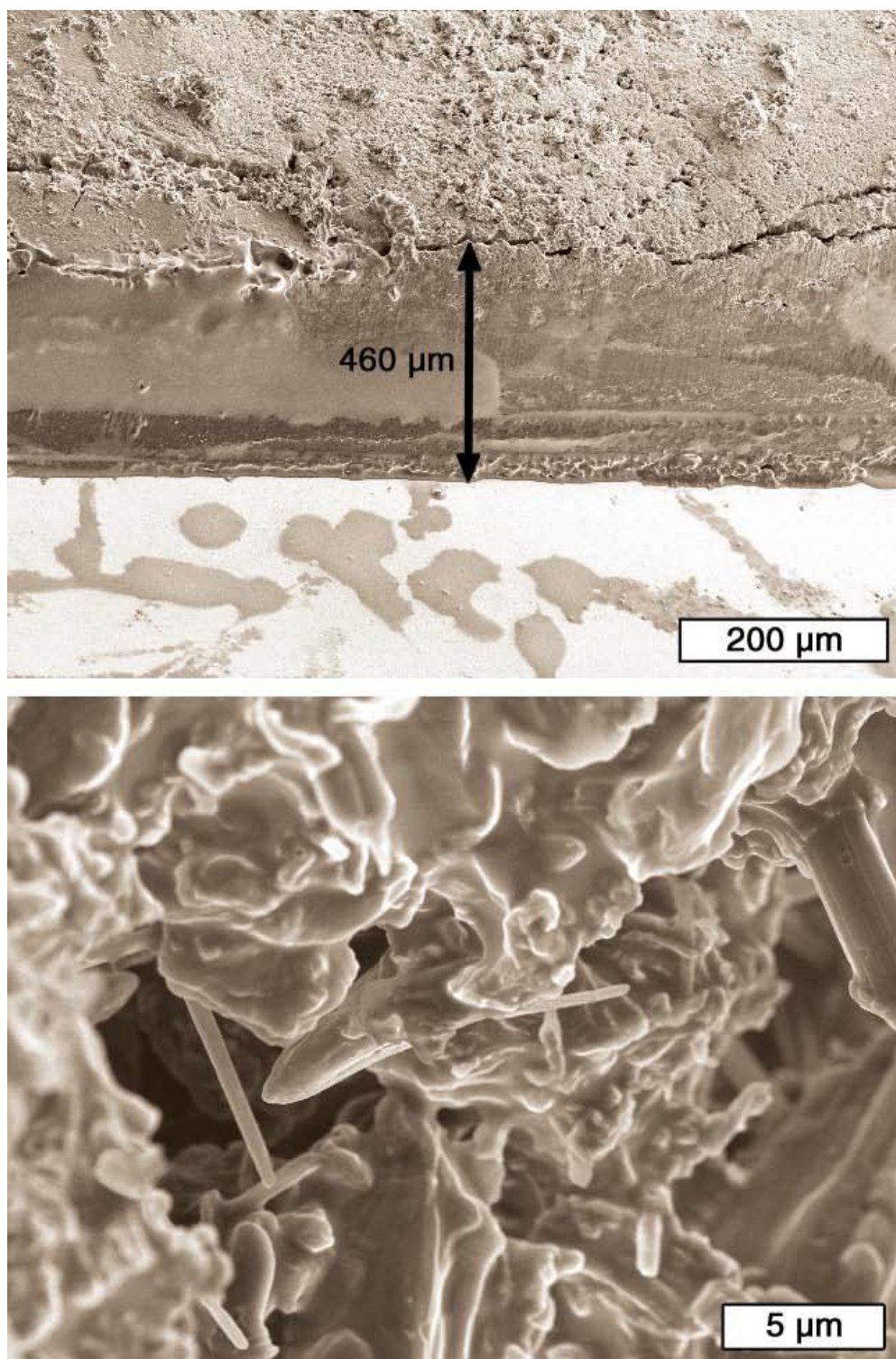


Figure S9. SEM images of lithium plating and stripping in conventional liquid electrolyte. SEM images of the stainless steel working electrode used in lithium plating and stripping experiments after 400 lithium plating and stripping cycles and imaged in the lithiated state at a 30° angle.

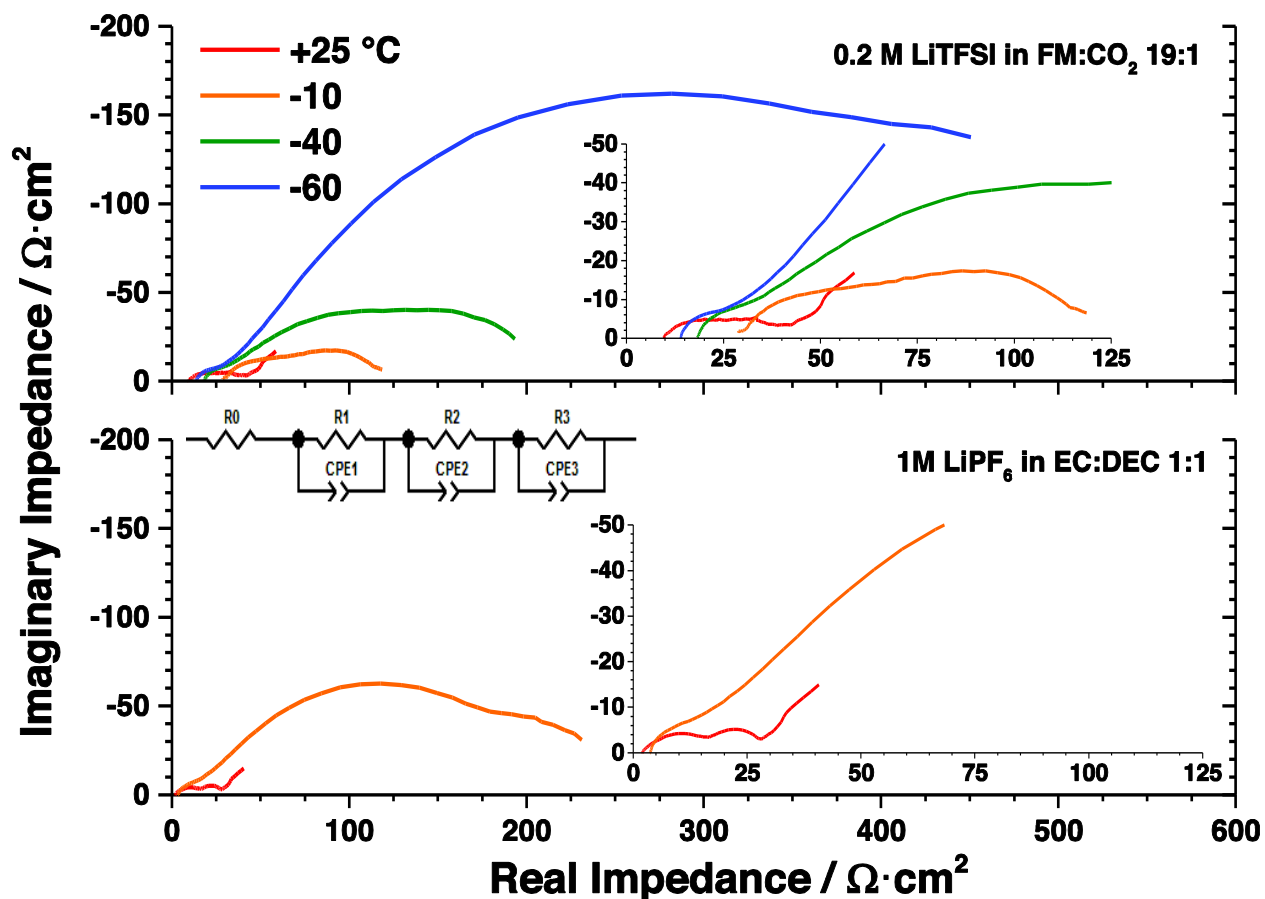


Figure S10. Electrochemical impedance spectra of lithium metal LiCoO₂ cell. Electrochemical impedance spectra of cells using LiCoO₂ and lithium metal as cathode and anode, respectively, with fluoromethane (top) and conventional liquid (bottom) based electrolytes. Spectra taken at a cell voltage of 4.1 V. Fitted impedance data is presented in **Table S3**. An additional RC circuit at high frequencies was an artifact of the wires and metal contacts submerged in the electrolyte solution due to the unique construction of the high pressure cells, thus the fitted parameter R₁ was held constant for each cell over all temperatures

Table S1. Ionization potential and electron affinity of liquefied gas solvents. Values for the ionization potential (IP) and electron affinity (EA) of various groups of solvents as calculated by DFT.

	Solvent	IP / eV	EA / eV
Liquid Solvents	Acetonitrile	12.21	-1.00
	Diethyl Carbonate	10.46	-1.30
	Dimethyl Carbonate	10.91	-1.27
	Ethyl Methyl Carbonate	10.66	-1.24
	Ethylene Carbonate	11.31	-1.19
	Fluoroethylene Carbonate	11.60	-0.86
	Tetrahydrofuran	9.33	-1.40
	Vinylene Carbonate	9.86	-0.96
Fluoromethanes	CH ₄	14.13	-1.87
	CH ₃ F	13.08	-1.66
	CH ₂ F ₂	13.12	-1.56
	CHF ₃	14.52	-1.48
	CF ₄	15.55	-1.48
Fluoroethanes	C ₂ H ₆	12.23	-1.83
	C ₂ H ₅ F	12.12	-1.62
	1,1-C ₂ H ₄ F ₂	12.45	-1.47
	1,2-C ₂ H ₄ F ₂	12.33	-1.45
	1,1,1-C ₂ H ₃ F ₃	14.14	-1.35
	1,1,2-C ₂ H ₃ F ₃	12.48	-1.44
	1,1,1,2-C ₂ H ₂ F ₄	13.25	-1.27
	1,1,2,2-C ₂ H ₂ F ₄	12.66	-1.73
	1,1,1,2,2-C ₂ H ₁ F ₅	13.30	-1.23
	C ₂ F ₆	14.07	-1.39
Fluoropropanes	C ₃ H ₈	11.50	-1.66
	CH ₂ FCH ₂ CH ₃	11.69	-1.50
	CH ₃ CHFCH ₃	11.65	-1.46
	C ₃ F ₈	13.33	-1.24
Fluoroethylenes	C ₂ H ₄	10.51	-1.74
	C ₂ H ₃ F	10.48	-1.81
	1,1-C ₂ H ₂ F ₂	10.57	-1.39
	1,2-cis-C ₂ H ₂ F ₂	10.02	-1.21
	1,2-trans-C ₂ H ₂ F ₂	10.42	-1.39
	C ₂ HF ₃	10.49	-1.21
	C ₂ F ₄	10.55	-1.13
Carbon Dioxide	CO ₂	13.84	-0.92

Table S2. Lithium metal submersion test results summary. Reactant characteristics resulting from soaking lithium metal in various solvents at +25 °C. Lithium metal disks of 0.04 cm thickness and 0.5 cm² were used. Lithium metal was soaked to reaction completion.

Solvent	Reaction Product	Approximate Reaction Speed	Product Color
Fluoromethane	Powder	20 days	Brown, Purple
Difluoromethane	SEI Formation	<1 min	No visible change
Fluoroethane	Powder	2 hours	White, Purple, Black
1,1-Difluoroethane	SEI Formation	5 minutes	Gray, Black
1,1,1,2-Tetrafluoroethane	SEI Formation	1 hour	Gray
2-Fluoropropane	Powder	3 hours	Purple, Black, White

Table S3. Impedance spectroscopy fitting parameters for lithium metal LiCoO₂ cells. Electrochemical impedance spectroscopy fitting parameters for cells using a lithium metal anode and LiCoO₂ cathode in two electrolytes over various temperatures. The fitted circuit and full impedance spectra are shown in Figure S10.

Electrolyte	Temperature / °C	Impedance / Ω·cm ²			
		R0	R1	R2	R3
0.2 M LiTFSI in FM:CO ₂ 19:1	+25	9.45	10.46	0.09	21.60
0.2 M LiTFSI in FM:CO ₂ 19:1	-10	28.50	10.46	25.10	58.40
0.2 M LiTFSI in FM:CO ₂ 19:1	-40	18.32	10.46	89.08	107.15
0.2 M LiTFSI in FM:CO ₂ 19:1	-60	13.35	10.46	579.00	124.90
1 M LiPF ₆ in EC:DEC 1:1	+25	1.84	11.10	3.03	14.36
1 M LiPF ₆ in EC:DEC 1:1	-10	3.49	11.10	27.58	212.71

Table S4. Global warming potentials of liquefied gas solvents. Global warming potentials (GWP) of selected liquefied gas solvents studied (69).

Solvent	100 Year GWP
Carbon Dioxide	1
Fluoromethane	92
Difluoromethane	675
Fluoroethane	12
1,1-Difluoroethane	124
1,1,1,2-Tetrafluoroethane	1430
2-Fluoropropane	N/A

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