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LETTER

Shear Thickening Electrolytes for High Impact Resistant Batteries

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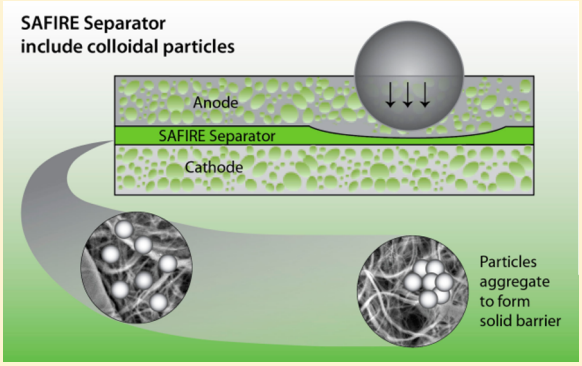
Supporting Information

ABSTRACT: We demonstrate a shear thickening electrolyte that stiffens into a solid-like barrier during a high energy event, like a car crash. This barrier prevents the electrodes from shorting during an impact, reducing the risk of fire or catastrophic safety events. In addition, we have demonstrated the ability to cycle NMC/graphite lithium ion cells over 200 cycles with no loss of capacity after formation. This chemistry introduces multi-functionality to a material previously feared due to its flammability.



In lithium ion batteries, the aprotic solvents in the electrolyte are a major safety concern due to their flammability.[1−5] Consequently, extensive chemical and engineering efforts are being undertaken to prevent internal electrical shorts or cell damage.[6] This work focuses on changing this paradigm by making the electrolyte an integral part of the cell safety in addition to its role in providing basic electrochemical performance. To accomplish this goal, we have developed an electrolyte that behaves like a liquid under normal operating conditions but undergoes shear thickening in response to shear stress. Upon shear thickening, the electrolyte behaves like a solid, which imparts the safety predicted for a solid-state electrolyte and prevents the internal electrical shorting that may lead to cell failure and fires. These SAFe Impact Resistant Electrolytes (SAFIRE) can be easily produced from low-cost and battery-compatible materials.

In the SAFIRE concept, inert particles are added to a standard battery electrolyte, for example, 1.2 M $LiPF_6$ 3:7 wt % ethylene carbonate/dimethyl carbonate, forming a dispersion. We have investigated silica as electrolyte additive inert particles. When silica is processed appropriately, it is stable in lithium ion batteries. Furthermore, it is well-known that silica in protic solvents like water and glycol shear thicken and has been demonstrated to stop projectiles, knives, and shivs.[7,8] Upon adding the electrolyte to the cell, it is likely that solvent and dissolved salt species are wicked into the electrode pores, leaving a higher concentration of silica particles suspended in solution between the working electrodes. The ceramic particles are relatively bulky and likely interact sparingly with the electrode surfaces.

Fumed silicas were obtained from commercial vendors (S5505, Aldrich; A300, Degussa; R972, Aerosil). Diatomaceous silica was purchased from Alfa Aesar. Stöber silica was prepared following the procedure reported by Bogush et al.[9] Briefly, tetraorthosilicate (Aldrich >99%) was added to 200-proof ethanol (chilled to 0 °C, Decon Chemicals), followed by deionized 18 MΩ water and ammonia hydroxide (JT Baker ACS grade). The precipitation reaction occurred over a couple of hours, resulting in a milky white suspension. The suspension was centrifuged, and the solution phase was poured off. The resulting powder was washed/centrifuged three more times with 200-proof ethanol. All of the powders were dried at 100 °C under vacuum for 18 h and transferred to an argon-filled glovebox. Electrolytes were formulated by mixing various weight fractions of the silica in 1.2 M $LiPF_6$ 3:7 wt % ethylene carbonate/dimethyl carbonate (BASF) using an ultrasonic wand.

Rheology measurements were used to evaluate the shear thickening response of various synthesized and commercially

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purchased silicas. Rheological measurements were carried out on the suspension with various solid loadings using a controlled stress rheometer (TA Instruments ARG2) fitted with a starch pasting cell. Various fumed silicas were dispersed in the electrolyte at concentrations between 5 and 30 wt %. Rheology data for these materials is shown in Figures S1−S4. These materials all started as a gel and underwent a shear thinning response, becoming less viscous in contrast to previous studies on fumed silica in nonaqueous electrolytes.[10] In addition, the electrolytes prepared using fumed silica all reacted, resulting in a red-colored electrolyte and the generation of a red gas that has not yet been identified. Care should be taken when working with these materials as the gas is highly corrosive, as evident by its ability to react with and destroy gas chromatograph septa (Supelco Thermogreen LB-2). Our present working hypothesis for the reactivity is the termination chemistry of the fumed silica, which likely differs from that of the other silicas used in this work and is consistent with the known variety of Si−O−H surface terminations[11] and the differences in fumed versus precipitated materials.[12]

In contrast, electrolytes prepared using Stöber[13]-derived and diatomaceous silica exhibited an immediate and obvious shear thickening response, as evident in the rheology data measured for these samples shown in Figure 1. This data shows the

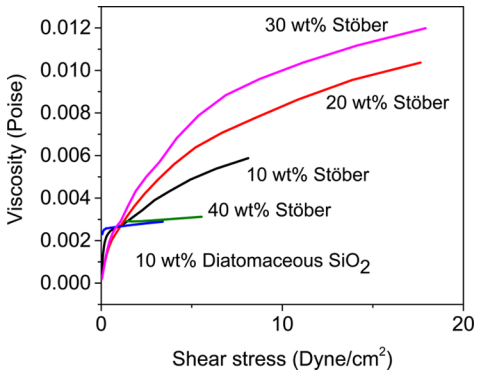

Figure 1. Viscosity as a function of shear stress for various SAFIRE electrolytes.

Table 1. Particle Dispersity As Measured with Light Scattering

shear thin or thicken	material	polydispersity
thin	S5505 fumed	0.156
thin	A300 fumed	0.495
thin	R972 fumed	0.16
thin	Stöber batch 16	0.243
thin	Stöber batch 20	0.187
thicken	diatomaceous silica	0.005
thicken	Stöber batch 06	0.087
thicken	Stöber batch 07	0.005
thicken	Stöber batch 21	0.005

immediate increase in viscosity with the application of shear. The magnitude of this response changes depending on the particle weight loading in the solvent such that there is a maximum response at a weight loading of about 30 wt %. This shear response results in the formation of an effectively solid layer, as evident in the video shown in the Supporting Information. This rheological response does not seem to be limited by the high concentration of Li^+ salt (up to 1.5 M) in

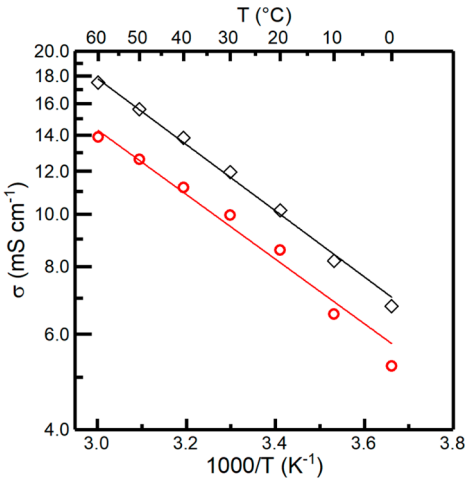

Figure 2. Ionic conductivity as a function of temperature for standard electrolyte and SAFIRE with 25 wt % Stöber silica.

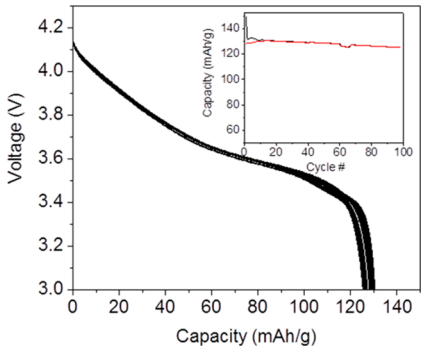

Figure 3. Discharge voltage as a function of capacity for a cell with 20 wt % Stöber silica. (Inset) Cell capacity as a function of cycle.

the electrolyte, which could have screened Coulombic repulsions between the particles causing flocculation.

To understand the differences in the shear responses between the various silicas, light scattering measurements were performed using a Brookhaven ZetaPALS instrument. The results are summarized in Table 1. It was found that highly monodisperse (<0.01) silica particles dispersed in electrolyte resulted in materials with a shear thickening response in aprotic solvents, while polydispersed particles (>0.1) exhibited shear thinning in aprotic solvents. These results point to a mechanism whereby highly uniform particles disperse in solution, forming a homogeneous mixture.[14] Under shear, this mixture likely rearranges, resulting in disordered or aggregated silica that blocks fluid flow.

The ionic conductivity of the electrolytes was measured at 20 °C using a frequency response analyzer (Solarton 1260). Drops of electrolyte were placed on top of gold interdigitated electrode arrays (ALS Company, Tokyo, Japan), and impedance was measured as a function of frequency from 1 MHz to 10 mHz. As the characteristic frequency of the electrolyte bulk was above 1 MHz, the impedance spectra were fit to an R_{DC}−Q_{DL} equivalent circuit, where R_{DC} is the DC resistance of the electrolyte bulk and Q_{DL} is a constant-phase element modeling the double-layer capacitance of the Au−electrolyte interface. Ionic conductivity (σ) was calculated using $\sigma = K/R_{DC}$, where the cell constant (K) of 0.0625 cm^{-1} was determined from the geometric attributes of the electrode array. The data comparing the samples with and without 25% Stöber

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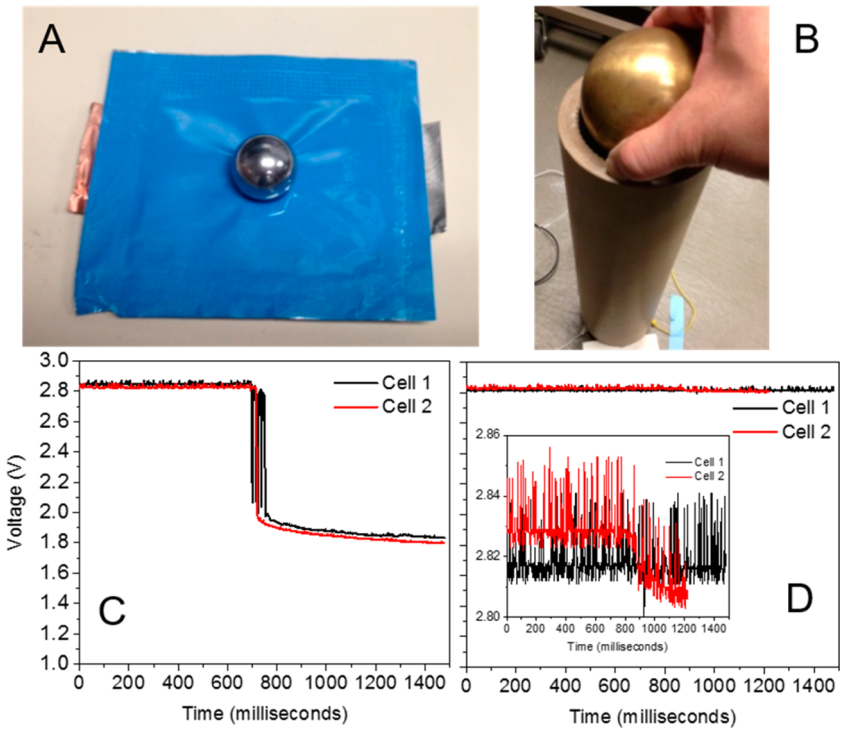

Figure 4. (A) Image of a stainless steel ball on a single-layer pouch cell. (B) Image of the brass ball used for the impact test. (C) Voltage stability results for the standard electrolyte. (D) Voltage stability results for the SAFIRE electrolyte.

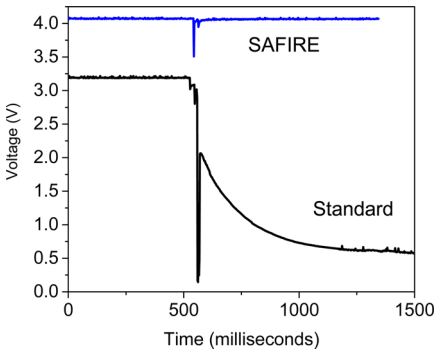

Figure 5. Voltage stability during impact with and without the SAFIRE electrolyte using a PEEK scaffold.

silica added to the electrolyte are shown in Figure 2. This shows the addition of silica results in a 25% decrease in ionic conductivity, but the activation energy remains the same (11.7 and 11.4 kJ/mol, respectively), as evident by the parallel lines, and the change in conductivity is consistent across the temperature range. This decrease in ionic conductivity is consistent with dilution of the electrolyte by an inert agent and would not affect cell performance for high-capacity batteries operated at low charge/discharge rates. Furthermore, conductivity could be increased with the addition of functional polymers, different anions, and the exploitation of "soggy-sand"-type effects.[15,16]

After identifying suitable shear thickening electrolytes, electrochemical cycling tests were performed. In these measurements, balanced cells were used consisting of a graphite anode (installed first) and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode with two high-porosity separators (DreamWeaver Gold 40) to give enough volume for the electrolyte to penetrate. Coin cell kits (Pred Materials) were assembled for electrochemical testing. The cells consisted of 16 mm disks of the graphite anode and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode. Electrolytes with 20 wt % silica were prepared using the Stöber silica. The 20 wt % solution was selected so that liquid electrolyte could fill the electrode pores, leaving the colloidal silica in suspension in a higher concentration (approaching 30 wt %). Given the rheological response of this material, it was impossible to accurately pipet this electrolyte; therefore, approximately 200 mg of electrolyte was added dropwise to the anode/separator stack and allowed to wet the entire separator. The cathode was added followed by sealing the coin cell. The cells were allowed to rest for 20 min before cycling. The cells were cycled at a rate of C/3 at 24 °C using a Maccor battery cycler (8000 Series). Pouch cells were constructed using the same anode/cathode combination and weight loadings of electrolyte using DreamWeaver or polyether ether ketone (PEEK) mesh (0.0086 in. opening, 0.0015 in. wire size, McMaster-Carr). Figure 3 shows representative cycling data collected for these cells, demonstrating that when processed properly the electrodes cycle well. The discharge data is in Figure S5. We found heating the silica to 100 °C under vacuum was critical to cell performance. The initial capacity loss on the first cycle is due to solid electrolyte interphase formation on the graphite electrode.

To evaluate the impact performance of these electrolytes, single-layer pouch cells were constructed using the same configuration and areal weight loading of the electrolyte explored in the coin cell studies. For these tests, a 1.27 cm diameter stainless steel ball was placed on the cell, Figure 4A. A 1.923 kg brass ball was positioned 43 cm above the stainless steel ball (Figure 4B) and dropped onto the cell. The impact energy, 5.65 Joule, of the brass ball was transferred to the stationary steel ball. The impact speed was estimated at 2.9 m/s. This energy is almost an order of magnitude larger than that from the previous report.[10] The combination of impact energy

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and steel ball curvature can induce a through-layer short circuit in test cells with regular electrolyte. To test the performance of the electrolyte on inactive pouch cells, two AA batteries (2.8–3.0 V) were connected in series with the test cell and a 1 Ohm current-limiting resistor. The voltage of the AA batteries was monitored constantly via a LabView program at a data acquisition speed of 100 Hz. When a short circuit occurred, the voltage dropped and discharged through the resistor. For live cells, the open-circuit voltage was monitored without additional batteries and a resistor.

Figure 4C shows the performance of two cells constructed using two separators and a standard BASF 1.2 M $LiPF_6$ 3:7 wt % ethylene carbonate/dimethyl carbonate electrolyte. Upon impact, there is a clear decrease in the cell voltage due to shorting. In contrast, Figure 4D shows the impact performance of two cells with the SAFIRE electrolyte. In this case, there is little to no change in the voltage upon impact, demonstrating that the electrolyte responded immediately, presumably forming hydroclusters of silica particles that increased the stiffness of the barrier separating the electrodes. To explore this improvement further and confirm that the improvement was truly due to the electrolyte, cells were constructed using a polyether ether ketone (PEEK) mesh (0.0086 in. opening, 0.0015 in. wire size, McMaster-Carr) as a scaffold to separate the electrodes. Note that this is not a standard separator but does provide a platform to evaluate if the shear thickening electrolyte actually works or if the commercial separator, cell packaging, or other components (Li-metal)[10] dominate or influence the impact resistance. The cells were filled with either standard or SAFIRE electrolyte and subjected to the same impact test (Figure 5). From this data, it is apparent that the cells with the standard electrolyte immediately and catastrophically shorted. There was a soft short in the SAFIRE cell that immediately recovered, and the cell returned to the original voltage. These results demonstrate the safety improvement gained from the use of shear thickening electrolytes. There is likely no benefit during slower events such as nail penetration or other smaller protrusions, such as Li-dendrites.

In summary, we have demonstrated a non-Newtonian electrolyte concept that can provide a significant increase in safety during a high-energy event using nonfumed, monodispersed silica. The electrolytes are effective during high-speed events where there is a rapid rearrangement of the colloidal particles. These electrolytes could provide significant safety improvements to high-energy batteries by preventing internal electrical shorts, for example, during a car accident.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00511.

Shear thickening video (MPG)
Viscosity measurements and cycling data (PDF)

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Notes

The authors declare no competing financial interest.

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