High transference number enabled by sulfated zirconia superacid for lithium metal batteries with carbonate electrolytes

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Article

Keywords: Lithium Metal Batteries, Dendrites, Solid-Electrolyte-Interphase, Superacid

Posted Date: September 10th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-73435/v1>

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Version of Record: A version of this preprint was published at Energy & Environmental Science on January 1st, 2021. See the published version at <https://doi.org/10.1039/D0EE03967E>.

Abstract

The prospect of increasing the energy density has promoted research on lithium metal batteries. Yet, avoiding the uncontrolled growth of lithium dendrites and the resulting interfacial instability to ensure the practical viability of the given battery technology remains a considerable challenge. Here, we report coating the separator with sulfated zirconia superacid to achieve a high lithium ion transference number of 0.92 and compelling cycle life when a full-cell paired with a $\text{LiNi}_0.82\text{Co}_0.07\text{Mn}_0.11\text{O}_2$ cathode was tested in a carbonate electrolyte under practical operating conditions. The exceptionally high transference number is attributed to strengthened binding of the PF_6^- anion of the lithium salt with the superacid. Furthermore, a trace amount of water bound to the superacid reacts with PF_6^- to induce a mechanically stable solid-electrolyte-interphase (SEI) layer rich in $\text{Li}_x\text{PO}_y\text{F}_z$. This study demonstrates the beneficial effect of the superacid on emerging post-lithium-ion batteries by immobilizing the anion of the salt as well as modifying the SEI composition.

Main Text

The emergence and fast growth of the electric vehicle market was enabled by the technological maturity of lithium-ion batteries (LIBs)^{1,2}. Particularly, a longer driving distance and increased charging speed played a central role in the widespread adoption of LIBs. Nonetheless, the search for new electrode materials has continued as the energy density of current intercalation-based electrode materials is clearly limited in terms of both their gravimetric and volumetric characteristics. The recent considerable attention^{3,4} devoted to lithium metal batteries (LMBs) similarly aimed to increase the energy density as metallic lithium (Li) has a redox potential of -3.04 V vs. the standard hydrogen electrode and a theoretical specific capacity of 3860 mAh g^{-1} or 2060 mAh mL^{-1} .

It is well accepted^{5,6} that the uncontrolled growth of Li dendrites imposes a formidable challenge that would need to be addressed to ensure the reversible and sustainable cycling of LMBs. In particular, when the charging current surpasses the so-called Sand's time, the Li-ion concentration at the electrode-electrolyte interface becomes depleted, thereby allowing dendrites to grow in an accelerated manner^{7,8}. This phenomenon indicates the importance of uniform and facile Li ion transport near the Li metal surface, and many reported approaches involving separator coating⁹⁻¹³, surface treatments of Li metal¹⁴⁻¹⁸, and the use of solid electrolytes with high ionic conductivities¹⁹⁻²³ can be understood in the same context. The solid electrolyte interphase (SEI) layer is also well accepted^{24,25} to play a crucial role in the interfacial stability during repeated Li plating and stripping. A mechanically weak SEI layer is vulnerable²⁶ to crack formation due to the build-up of stress in the Li deposits underneath. Once the SEI layer breaks down owing to further stress accumulation, the Li deposit could protrude from the layer in the form of dendritic growth. In addition, it is worth keeping in mind that the cell configurations and manufacturing schemes of existing LIBs are preferred when any new approaches are implemented. In this regard, carbonate-based electrolytes are desirable²⁷⁻²⁹ over others because the cathodes to be paired with Li metal electrodes have been developed on the basis of these electrolytes. However, unfortunately, the

levels of the lowest unoccupied molecular orbitals (LUMOs) of carbonates are sufficiently low^{30,31} to induce facile reductive decomposition and consequently a weak irregular organic-dominant SEI layer.

Li ion transport in a liquid electrolyte is affected by multiple parameters including salt dissociation, the degree of solvation, and the viscosity of the solvent, and these parameters are often interrelated to each other. Moreover, Li ion transport and the spatial distribution thereof at the interface are largely influenced by the physicochemical properties of the SEI layer, and the composition of this layer can affect Li nucleation and subsequent growth behavior^{32,33}. This rationale led us to pursue an approach by which the dissociation of the Li salt is tuned to obtain a high Li ion transference number, and the dissociated anion can yield an SEI layer with high stability upon reaction with the electrolyte solvents. In this vein, we adopted sulfated zirconia (denoted as S-ZrO₂) because S-ZrO₂ can function as a solid acid to promote the dissociation of the Li salt most commonly used in LIBs, namely lithium hexafluorophosphate (LiPF₆), by strongly binding with the PF₆⁻ anion. A solid acid is a class of superacid and exhibits extremely high acidity, even several orders of magnitude higher than that of pure sulfuric acid. The extraordinary acidity of S-ZrO₂ arises^{34,35} from the inductive effect of the sulfate complex with its high electron-withdrawing ability, which enhances the affinity of the superacid for a Lewis base. We applied a coating of S-ZrO₂ superacid nanoparticles to the separator with the aim of distributing the superacid effect over the entire electrode area while simultaneously benchmarking the concept of a ceramic nanoparticle coating to minimize the thermal shrinkage that commercial LIBs are prone to experience at high temperatures. This approach enabled the transference number to reach a value as high as 0.92 as a result of the superacid effect, and this, along with the modified SEI layer involving liberated PF₆⁻ anions, resulted in highly reversible and sustainable cyclability of the Li plating-stripping process. In previous studies, solid superacids were implemented³⁶⁻³⁸ in polyethylene oxide (PEO) polymer electrolytes to improve the ionic conductivity or transference number; however, they have not been used in liquid-based cells at all. The present investigation points to the unique advantage offered by superacids: simultaneously high values for both ionic conductivity and transference number, unlike solid-state electrolytes that have a high transference number but are affected by moderate ionic conductivity particularly at the interface, and, needless to mention, poor processability. These beneficial properties are rooted in the physical state of superacid solids; i.e., being solid in nature but functioning in the liquid state.

Synthesis and Coating of Sulfated Zirconia Superacid

The S-ZrO₂ nanoparticles were synthesized *via* a sol-gel process. Briefly, 1.0 M zirconium *n*-propoxide in anhydrous *n*-propanol was hydrolyzed in a mixture of sulfuric acid and distilled water, followed by condensation at 50 °C for 1 hour. The compound in the gel state was washed with anhydrous ethanol and centrifuged to accomplish dehydration. Finally, the centrifuged sample was calcined at 600 °C for 3 hours. Details of the synthetic procedure are provided in the Methods Section. X-ray diffraction (XRD) analysis (Figure 1a) showed that the synthesized compound had a single tetragonal phase belonging to the P4₂/nmc space group (ICSD collection code = 66787) without impurities. The FTIR profile of the S-ZrO₂ exhibited peaks at 1213, 1130, 1041, and 995 cm⁻¹ (Figure 1b), which were

assigned³⁹ to the sulfate ion coordinated to Zr^{4+} in a bidentate configuration. Thermo-gravimetric analysis (TGA) indicated that the sulfate anion content is 10.0 wt% (Supplementary Figure 1). In addition, the N_2 adsorption-desorption isotherm of S-ZrO_2 revealed its surface area to be $104 \text{ m}^2 \text{ g}^{-1}$, and its primary particle size to be in the range 5–10 nm, as visualized by scanning electron microscopy (SEM) (Figure 1c). After measuring the transference number and assessing the cycling performance with a Li-Li symmetric cell setting by varying the sulfate contents in the range of 2–10 wt% (Supplementary Figure 2), the sample with sulfate content of 10 wt% was chosen as the main sample for subsequent experiments.

The polyethylene (PE) separator was coated with the prepared S-ZrO_2 nanoparticles *via* a simple doctor blading process. The coating was uniformly spread across the entire separator (Figure 1d) to obtain a thickness of 3–4 μm (Figure 1e). As in the current LIB technology, the S-ZrO_2 coating serves another purpose namely to ensure the mechanical stability of the membrane against thermal shrinkage. The thermal stability test involved maintaining the separator at 125 °C for 1 hour, and the S-ZrO_2 -coated film was observed to preserve 92.6% of its original dimension, in contrast with the 78.7 % retention of the bare PE film (Supplementary Figure 3), indicating that the S-ZrO_2 coated separator offers superior mechanical resistance against high temperature.

Symmetric Cell Test and Electrode Analysis

The effect of the superacid S-ZrO_2 on the Li plating and stripping behavior was examined by conducting galvanostatic tests using a Li-Li symmetric cell configuration. For comparison, cells containing the bare PE separator and ZrO_2 -coated separator were also evaluated in parallel. When scanned at a current density of 3.0 mA cm^{-2} for 1 hour for each Li plating and stripping, the voltage profile of the bare PE cell surpassed $\pm 0.4 \text{ V}$ after 90 cycles (Figure 2), reflecting⁴⁰ uncontrolled SEI growth and subsequent electrolyte depletion. The ZrO_2 -coated cell extended the cycling slightly and began to surpass $\pm 0.4 \text{ V}$ after 96 cycles. After these points of extremely high overpotentials, these two cells ceased to operate. By contrast, the cycling of the S-ZrO_2 -coated cell was sustained much longer such that its overpotential surpassed $\pm 0.4 \text{ V}$ after 821 cycles. The trend among the cells was translated even when the current density was raised to 6.0 mA cm^{-2} for a duration of 0.5 hour for each Li plating and stripping (Supplementary Figure 4), except that the onset point of voltage fluctuations for the S-ZrO_2 -coated cell was dragged to around the 559th cycle owing to the higher current density. In the same context, the S-ZrO_2 -coated cell exhibited more sustainable cyclability in an asymmetric cell setting in which copper (Cu) foil was used as one of the electrodes (Supplementary Figure 5).

The effect of the S-ZrO_2 superacid coating on the morphology of the Li deposit was investigated using SEM after the 1st and 100th Li plating when galvanostatically scanned at 3.0 mA cm^{-2} for 1 hour for each Li plating and stripping (Figure 3). Even after the 1st charge, the bare PE and ZrO_2 -coated cells showed extensive growth of Li dendrites with high aspect ratios according to their top-view images

(Figure 3a and b, first two images), and the thicknesses of the Li plated layers were 63 and 47 μm , respectively (Figure 3a and b, rightmost images), owing to indiscriminate growth of the SEI layer. By contrast, the S-ZrO₂-coated cell showed a more compact and distributed Li plated layer with rounded morphology of individual Li deposits (Figure 3c, first two images). The thickness of the Li plated layer was only 39 μm (Figure 3c, rightmost image). The difference among the cells became more pronounced after the 100th charge. The growth of sharp Li dendrites continued in the bare PE and ZrO₂-coated cells (Figure 3d and e, first two images), but most of them could barely be observed because of indiscreet coverage by the SEI layer. The uncontrolled growth of the SEI layer was reflected in the significantly increased thicknesses of the Li plated layers to 250 and 170 μm , respectively (Figure 3d and e, rightmost images). Contrary to this observation, the S-ZrO₂-coated cell preserved the compact morphology of its Li deposit (Figure 3f, first two images), increasing the thickness of the Li plated layer to only 46 μm (Figure 3f, rightmost image). Thus, it can be concluded that the improved cyclability resulting from the S-ZrO₂-coating observed in Figure 2 is associated with the morphology of the Li deposit, which has a direct impact on the interfacial stability.

Full-Cell and Other Electrochemical Tests

The reversibility and sustainability of the bare PE, ZrO₂-coated, and S-ZrO₂-coated cells were also evaluated in a full-cell setting paired with LiNi_{0.82}Co_{0.07}Mn_{0.11}O₂ cathodes (Figure 4). Notably, Li foil with a thickness of 40 μm was used for testing with a relatively practical n/p ratio of 3.0. As displayed in Figure 4a, the bare PE, ZrO₂-coated, and S-ZrO₂-coated cells exhibited almost identical charge-discharge profiles in their respective 1st cycles in which an average redox voltage of 3.8 V and specific capacity of 203.6 mAh g⁻¹ with respect to the cathode weight were observed when scanned at 0.1C rate (1C= 200.0 mA g_{cathode}⁻¹), implying that the S-ZrO₂ coating on the separator did not alter the full-cell chemistry.

The cyclability of the S-ZrO₂-coated full-cell was conspicuously more robust compared to that of the bare PE and ZrO₂-coated full-cells. Upon cycling at 1C (3.0 mA cm⁻²), the S-ZrO₂-coated full-cell maintained 83.0% of its initial capacity after 150 cycles (Figure 4b), whereas the bare PE and ZrO₂-coated full-cells preserved 25.2% and 23.0% of their initial capacities after the same number of cycles, respectively. The rapid decrease in the capacity of both the bare PE and ZrO₂-coated full-cells was also reflected in their Coulombic efficiency (CE) profiles (Figure 4c). These series of data verify that the superior cyclability obtained with the S-ZrO₂ superacid coating is valid in a practical full-cell setting.

The effect of the separator modifications on the ionic conductivity of Li was assessed by carrying out electrochemical impedance spectroscopy (EIS) analysis (Supplementary Figure 6a). The x-intercepts of the EIS profiles reveal that the ionic conductivities of the bare PE, ZrO₂-coated, and S-ZrO₂-coated cells are 0.64, 0.51, and 0.49 mS cm⁻¹, respectively (Figure 5a), indicating that the application of ZrO₂ and S-ZrO₂ coatings did not change the ionic conductivity markedly. Moreover, the three cells were subjected to

5 mV bias for 12 hours to monitor the impedance change until they reached the steady state (Supplementary Figure 6b). These measurements were used to retrieve the transference numbers (Figure 5b) based on the equation^{41,42}:

$$t_{Li^+} = \frac{I_{ss} \times (\Delta V - I_0 \times R_0)}{I_0 \times (\Delta V - I_{ss} \times R_{ss})}$$

where, I_{ss} , I_0 , R_{ss} , R_0 , and ΔV represent the Li-ion transference number, steady-state current, initial current, steady-state resistance, initial resistance, and applied voltage (5 mV), respectively. Notably, the transference number of the S-ZrO₂-coated cell increased dramatically to 0.92 from 0.36 for the bare PE cell and 0.38 for the ZrO₂-coated cell, implying that the superacidity of S-ZrO₂ enhances the migration of Li⁺ exclusively from the PF₆⁻ anion. Notably, this transference number is higher than those of any liquid-based Li cells reported to date^{43,44}, including the implementation⁴⁵ of a metal-organic framework (MOF) layer (= ~0.7) in which anionic sub-nanometer channels screen anions in the electrolyte.

Origin of High Li⁺ Transference Number

Raman and ³¹P solid NMR analyses were carried out to determine the origin of the high Li⁺ transference number of the S-ZrO₂-coated cell. The Raman analysis (Figure 6a) unveils the dissociative nature of the LiPF₆ salt and its interaction with the solvent. This analysis entailed examining the carbonate electrolyte (1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC), 3:7=v:v with 10 vol% fluoroethylene carbonate (FEC)) after soaking the bare PE, ZrO₂-coated, and S-ZrO₂-coated separators in the electrolyte for 24 hours. The Raman spectra of the three samples exhibited similar peak intensities at 728 cm⁻¹, related⁴⁶ to Li⁺-EC interaction, indicating that the solvation environment of the Li⁺ ion with EC was not perturbed significantly by the addition of the S-ZrO₂ superacid. However, the peak intensity of the free PF₆⁻ anion at 741 cm⁻¹ relative to that of the free EC peak at 716 cm⁻¹ decreased for the S-ZrO₂-coated separator compared with the bare PE and ZrO₂-coated separators (intensity ratio: 0.82 vs. 0.97 vs. 0.94). This observation reveals the Lewis acid-base interaction between the S-ZrO₂ superacid and PF₆⁻, providing the reason for the increased Li⁺ ion transference number in the case of the S-ZrO₂-coated separator. In a similar context, the ³¹P solid NMR spectrum of the S-ZrO₂ soaked in the electrolyte exhibited a band in the range -10 ~ -30 ppm corresponding to the PO_yF_{6-y}^{δ-} anion⁴⁷, which was barely observed for the ZrO₂ counterpart and was not observed at all for bare LiPF₆. The appearance of this band is attributed to the reaction of the PF₆⁻ anion bound to S-ZrO₂ with a trace amount of water. This role of the S-ZrO₂ superacid is indeed analogous to the way in which S-ZrO₂ offers superacidity: the Lewis acid sites in the S-ZrO₂ superacid attract electron-donating groups (Supplementary Figure 7).

Effect of Sulfated Zirconia on the SEI Properties

The modified potentiostatic intermittent titration (PITT) technique was employed to examine the electrolyte decomposition behavior at different potentials below the Li/Li^+ standard potential (Figure 6c). This analysis was conducted by decreasing the potential in decrements of 2 mV and maintaining the potential at each decremental level for 1 hour to record the electron consumption. In both cells, electrolyte decomposition was observed in the potential range of $-8 \sim -30$ mV vs. Li/Li^+ before Li deposition was detected below -32 mV with far greater electron consumption. Notably, the amount of electron consumption used for electrolyte decomposition was substantially larger for the S-ZrO_2 -coated cell compared with the bare PE cell, revealing that SEI formation was more prominent in the S-ZrO_2 -coated cell at higher potentials. Computational calculations were conducted to elucidate the augmented SEI formation in the S-ZrO_2 -coated cell (Figure 6d). We estimated the energy levels of the lowest unoccupied molecular orbital (LUMO) of the PF_6^- anion, its derivatives upon reaction with water (i.e., PO_xF_y), and the carbonate solvents included in the electrolyte. According to the results, the first oxidized form of PF_6^- , POF_3 , has a lower LUMO energy level compared to those of the carbonate solvents. Considering that the LUMO energy level generally represents a reduction priority, our results suggested that the POF_3 formed at the surface of S-ZrO_2 serves as the origin of the prominent electrolyte decomposition of the S-ZrO_2 -coated case.

Furthermore, the onset potential for Li deposition was approximately 14 mV higher for the S-ZrO_2 -coated cell compared with the bare PE cell (-32 vs. -46 mV) (Figure 6c), inferring^{48,49} that the modified SEI layer lowers the activation energy for Li deposition. Additionally, the SEI layer of the S-ZrO_2 -coated cell proved to be more robust than that of the bare PE cell (Supplementary Figure 8). When the symmetric cells were left standing for a different number of days after one cycle of Li plating and stripping, the increase in the semicircle of the EIS profile was much more prominent for the bare PE cell (Supplementary Figure 8a) compared with that of the S-ZrO_2 -coated cell (Supplementary Figure 8b), pointing to inferior SEI stability in the bare PE case.

The effect of the S-ZrO_2 superacid on the SEI composition was studied by X-ray photoelectron spectroscopy (XPS). The XPS spectra of the S-ZrO_2 superacid before and after its immersion in the electrolyte for 24 hours were compared for the $\text{Zr } 3d$, $\text{O } 1s$, $\text{S } 2p$, $\text{P } 2p$, and $\text{F } 1s$ branches (Supplementary Figure 9). After immersion, new peaks appeared at higher binding energies of 187.6, 533.5, and 170.8 eV in the $\text{Zr } 3d$, $\text{O } 1s$, and $\text{S } 2p$ branches, respectively, which could likely be attributed to $\text{Zr-PO}_y\text{F}_z$, P-O-F^{50} , and S-O in the sulfate. However, further investigation is needed as the peaks at 187.6 and 170.8 eV were unidentified in the literature. At the same time, a combined analysis of the profiles in the $\text{P } 2p$ and $\text{F } 1s$ branches indicates the formation of PO_yF_z^- , which is once again commensurate with the aforementioned observation related to the reaction of a trace amount of water with PF_6^- bound to the S-ZrO_2 superacid. When XPS analysis preceded by 300 seconds of etching was performed for Li metal electrodes after the 1st Li plating (Supplementary Figure 10), the peak of the $\text{F } 1s$ branch appeared at 687.2 eV and the peaks

of the P 2p branch were observed at 136.2 and 134.1 eV. This revealed an SEI composition containing $\text{Li}_x\text{PO}_y\text{F}_z$, which is consistent with that of the immersed S-ZrO₂ superacid described above, along with the fact that the interior of the SEI layer is rich in inorganic components. It should be noted that the complete removal of trace water from most carbonate electrolytes is impossible. In our experiment, the formation of PO_yF_z^- was preserved even after the electrolyte was stored over molecular sieves to reduce the amount of trace water, implying that the observed effect of the S-ZrO₂ superacid on the SEI composition is consistent regardless of the amount of trace water present in typical carbonate electrolytes. In addition, the XRD profiles of S-ZrO₂ remained unchanged (Supplementary Figure 11), thus supporting the catalytic role of the S-ZrO₂ superacid in increasing the transference number of the Li ion as well as inducing the PO_yF_z -rich SEI layer.

Conclusion

Interfacial stability is of key importance for the reliable operation of Li metal anodes and is greatly affected by the Li ion transference number and SEI characteristics. In spite of the widely accepted consensus in this regard, achieving the desired properties related to these parameters without sacrificing the volumetric energy density is no trivial matter; for instance, the integration of additional components that increase the Li ion transference number is mostly foreign to the current LIB technology and therefore demerits the use of a Li metal anode after comprehensive evaluation.

In this sense, the approach introduced in the present study, namely the incorporation of the S-ZrO₂ superacid, is effective yet realistic because the application of a coating of ceramic material to the separator is being adopted in most of the cells that are currently commercially available. Moreover, the effect of the given approach is substantial as the S-ZrO₂ superacid enhances binding with the anion of the Li salt, which increases the mobility of the Li ion apart from inducing a more stable SEI layer. While this view of the superacid-anion interaction was supported by Raman and ³¹P NMR analyses, its outcome was electrochemically validated in both symmetric- and full-cell configurations. Taking a broad perspective, the solid-state nature of the superacid warrants its easy integration into a cell and we thus foresee the universal applicability of the positive effects of the superacid to a wide range of rechargeable batteries beyond LMBs.

Methods

Synthesis of sulfated ZrO₂ superacid and ZrO₂ particles. 70 wt% zirconium *n*-propoxide (Sigma-Aldrich) in 20 mL of propanol (Sigma-Aldrich) was first mixed with 62.2 mL of anhydrous *n*-propanol (99.7% purity, Sigma-Aldrich). To this solution, 1.10 mL of sulfuric acid (99.999% purity, Sigma-Aldrich) and 14.81 mL of distilled water were added sequentially for 10 min at 50 °C until the vortex disappeared. The solution was then aged at the same temperature for another hour. Next, 100 mL of ethanol ($\geq 99.5\%$, Sigma-Aldrich) was added and the solution was centrifuged at 6000 rpm for 10 min to switch the solvent from water to alcohol to minimize particle growth during drying and calcination. This washing *via*

centrifugation was repeated three times. The produced powder was dried at 80 °C for 12 hours to remove residual alcohol, followed by calcination at 600 °C for 3 hours to produce the designated crystal structure. For S-ZrO₂ with 2 and 6 wt% sulfate, the same procedure was adopted except that 0.28 and 0.55 mL of sulfuric acid was added, respectively. The bare ZrO₂ particles were synthesized based on the same procedure as S-ZrO₂ particles except that sulfuric acid was not added.

Coating of S-ZrO₂ and ZrO₂ particles on the separator. The PE separator (16 µm thick, Toray) was coated with the synthesized S-ZrO₂ and ZrO₂ particles by using the doctor blading technique with 33 wt% S-ZrO₂ or ZrO₂ solution. The areal loading was 1.0 mg cm⁻² in both cases. For the thermal shrinkage test, separators with dimensions of 4.0×4.0 cm² were left in an oven at 125 °C for 1 hour and the dimensional changes were measured.

Electrochemical analysis. The symmetric cell tests were conducted by sandwiching various polyethylene separators between two sheets of Li foil (200 µm thick, Honjo Metal Co., Ltd.) and galvanostatically cycled at 3.0 or 6.0 mA cm⁻². Each charge or discharge was continued for 1 hour in the case of 3.0 mA cm⁻² and 0.5 hour in the case of 6.0 mA cm⁻². The electrolyte was 1 M LiPF₆ in EC/DEC (v/v=3/7) with 10 vol% FEC. The cells that were used for the asymmetric cell tests were prepared by using the same procedure except that one side of the electrodes was replaced by Cu foil. For the full-cell tests, LiNi_{0.82}Co_{0.07}Mn_{0.11}O₂ cathodes were fabricated by first preparing a slurry consisting of the active material, Super P, and poly(vinylidene difluoride) (PVDF) in a weight ratio of 96:2:2 in *N*-methyl-2-pyrrolidone (NMP). The slurry was cast onto Al foil *via* the doctor blade method and dried at 120 °C for 12 hours. The areal loading of the active material was 15.5 mg cm⁻². The Li metal foil on the anode side was 40 µm thick. The electrolyte was the same as that used in the symmetric cells. The full-cells were pre-cycled at 0.1C and cycled at 1C (1C=200 mA g_{NCM}⁻¹) in subsequent cycles. The amount of the electrolyte was 80 µL for each coin cell. Both symmetric and full-cells were prepared in the form of 2032 coin cells by assembling the anode, cathode, and separator in a dry room. The ionic conductivity of each separator was assessed by performing EIS analysis, which was carried out in the frequency range of 10⁻²–10⁶ Hz with an amplitude of 10 mV. The ionic conductivity was retrieved from the *x*-axis intercept of each profile. The transference number was obtained by monitoring the change in the current when subjected to an applied voltage based on the following relation^{41,42}:

$$t_{Li^+} = \frac{I_{SS} \times (\Delta V - I_0 \times R_0)}{I_0 \times (\Delta V - I_{SS} \times R_{SS})}$$

where I_{SS} is steady state current, I_0 is initial current, R_{SS} is steady state resistance, R_0 is initial resistance, and ΔV is voltage applied (5 mV in the current study). Modified PITT analysis was conducted by applying constant voltage for one hour at every 2 mV while the current was monitored. The measured potential ranged from 0 to -50 mV vs. Li/Li⁺. To test the stability of the SEI layer, EIS analysis was performed after leaving the symmetric cells for a different number of days after undergoing one cycle of Li plating and

stripping (C-rate=0.1C, capacity of each plating and stripping=3 mAh). These measurements were recorded in the frequency range of 10^{-2} – 10^6 Hz with an amplitude of 10 mV.

Characterization of S-ZrO₂ and ZrO₂ particles. XRD (Empyrean, PANalytic) and FTIR (VERTEX 70, Bruker) analyses were carried out to characterize the crystal structures and chemical bonds of the S-ZrO₂ and ZrO₂ particles, respectively. TGA (TG/DTA 6300, PerkinElmer) was used to evaluate the sulfate content in S-ZrO₂. SEM analysis (JSM-7000F, JEOL) was performed to visualize the morphology of the Li metal deposits on the surface. Raman analysis with a laser excitation wavelength of 532 nm (Senterra Grating 400, Bruker) was carried out for the electrolytes in which the different separators were soaked for 24 hours to monitor the ion-to-solvent interaction. ³¹P solid NMR analysis (ASCEND, Bruker) was conducted for the S-ZrO₂ and ZrO₂ particles soaked in the electrolyte for 24 hours. The conditions for ³¹P solid NMR analysis were such that the spinning frequency, dwell time, pre-scan delay, recycle delay, excitation pulse length, and excitation pulse power were 11 kHz, 6.3 msec, 6.3 msec, 0.5 sec, 5.0 msec, and 50 W, respectively. XPS (Scientific K-ALPHA, Thermo Fisher) was used to elucidate the SEI components.

DFT calculation. Geometrical optimizations and energy calculations were performed without symmetry restriction using the B3LYP hybrid density functional implemented in the GAUSSIAN 09 software package⁵¹. The 6-311+G(d, p) basis sets were adopted for all the atoms. Frequency calculations at the same basis sets were performed to determine the nature of a stationary point as a true local minimum.

Declarations

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

Acknowledgements

We acknowledge the support by the L&F Co.'s World Class 300 Project of the Korea Institute of Advancement of Technology (KIAT) funded by the Ministry of Trade, Industry, and Energy & Ministry of SMEs and Startups (No. S2483103) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (NRF-2018M1A2A2063353, NRF-2018M1A2A2063340 and NRF-2018R1A2A1A19023146).

Author contributions

S.-G.W., J.-S.Y., and J.W.C. designed the research. S.-G.W., E.-K.H., H.-K.K., H.L., J.-N.L, G.J., J.L., and S.K. performed the experimental work. D.-J.Y. performed the DFT calculations. S.-G.W., J.-S.Y., and J.W.C. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information is available online. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to J.-S.Y. and J.W.C.

Competing interests

The authors declare no competing financial interests.

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Figures

Figure 1

Synthesis and coating of S-ZrO₂ particles. a-b, (a) XRD and (b) FTIR profiles of S-ZrO₂ particles. c, SEM images of S-ZrO₂ particles. d, Digital photograph of PE separator coated with S-ZrO₂ particles. e, Top-view and cross-sectional SEM images of the coating of S-ZrO₂ particles on the PE separator.

Figure 2

Symmetric cell testing. Voltage profiles of the bare PE, ZrO₂-coated, and S-ZrO₂-coated symmetric cells when galvanostatically scanned at 3.0 mA cm⁻² for 1 hour for each Li plating and stripping.

Figure 3

Morphology of lithium deposit at 1st and 100th cycle. a-c, Top-view and cross-sectional SEM images after the 1st Li plating at 3.0 mA cm⁻² for 1 hour: Li electrodes of (a) PE_{reference}, (b) ZrO₂-separator,

and (c) S-ZrO₂-separator cells. d-f, Top-view and cross-sectional SEM images after the 100th Li plating at 3.0 mA cm⁻² for 1 hour: Li electrodes of (d) PE_{reference}, (e) ZrO₂-separator, and (f) S-ZrO₂-separator cells.

Figure 4

Full-cell testing when paired with the LiNi_{0.82}Co_{0.07}Mn_{0.11}O₂ cathode. a–c, (a) Initial voltage profiles, (b) capacity retentions, and (c) Coulombic efficiencies of the bare PE, ZrO₂-coated, and S-ZrO₂-coated

full-cells when paired with $\text{LiNi}_{0.82}\text{Co}_{0.07}\text{Mn}_{0.11}\text{O}_2$ cathodes. The C-rates in (a) and (b-c) are 0.1C and 1C, respectively ($1\text{C} = 200.0 \text{ mA g}_{\text{cathode}}^{-1}$).

Figure 5

Li ion transport behavior with different separators. a, Ionic conductivities of the bare PE, ZrO₂-coated PE, and S-ZrO₂-coated PE separators. b, Li ion transference numbers of the same three separators.

Figure 6

Effect of S-ZrO₂ superacid on ion dissociation and SEI composition. a, Raman spectra of the electrolyte after soaking the bare PE, ZrO₂-coated PE, and S-ZrO₂-coated PE separators in the electrolyte for 24 hours. b, ³¹P solid NMR spectra of the S-ZrO₂ and ZrO₂ after soaking in the carbonate electrolyte along with the profile of bare LiPF₆. c, PITT profiles of the bare PE and S-ZrO₂-coated cells for an applied potential below that of Li/Li⁺. d, LUMO energy levels of PF₆⁻, its derivatives, and the carbonate solvents.

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