High-conductivity Hydrophobic Fumed-SiO$_2$ Composite Gel Electrolyte for High Performance Electrochromic Devices

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Abstract: Gel electrolytes are chemically stable, nonflammable and easy to encapsulate, however, their moderate ionic conductivity ($10^{-4}$–$10^{-5}$ S·cm$^{-1}$) hinders their further development for use in electrochromic devices (ECDs). Here, we developed a highly conductive hydrophobic SiO$_2$/PMMA/PC/LiClO$_4$ gel polymer electrolyte (H-SiO$_2$ GPE). The electrochemical behaviors of ECDs were characterized by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and chronomperometry (CA). Systematic analyses indicate that the ionic conductivity of the H-SiO$_2$ GPE can reach $5.14 \times 10^{-3}$ S·cm$^{-1}$ (at 25 °C) by introducing only 0.5wt% hydrophobic fumed SiO$_2$. This increase is due to the good compatibility and hydrophobic-hydrophobic attractions between SiO$_2$ additive and organic electrolyte, which promotes the dissociation of lithium perchlorate. Additionally, the viscosity as a function of shear rate for GPE with various fumed silica contents shows the behavior of shear thinning, which indicates the formation of a three-dimensional network structure. This structure provides ion transport channels, leading to a clearly improved switching speed for ECDs assembled with hydrophobic SiO$_2$ GPEs ($\tau_{\text{bleaching}} = 4 \text{ vs } 8 \text{ s and } \tau_{\text{charging}} = 14 \text{ vs } 16 \text{ s}$). Similarly, the investigation of hydrophobic fumed SiO$_2$ in liquid electrolyte is demonstrated that the ionic conductivity of LiClO$_4$/PC liquid electrolyte without and with hydrophobic fumed SiO$_2$ increases from $6.94 \times 10^{-3}$ to $7.58 \times 10^{-3}$ S·cm$^{-1}$, respectively. Therefore, hydrophobic fumed SiO$_2$ as a filler has a positive effect on electrolytes, and the proposal of the H-SiO$_2$ GPE provides a new idea for offsetting the trade-off between a high ionic conductivity and easy leakage when applied in ECDs.

Key words: gel electrolyte; electrochromic; hydrophobic; SiO$_2$

Electrochromic devices (ECDs) can reversibly change their light transmittance via external voltage-induced redox reactions, and show potential applications in smart windows, electrochromic displays, switching mirrors, sensors, supercapacitors and so on$^1$. To stabilize ECDs, the internal resistance of ECDs must be remarkably reduced, which requires an ionic conductivity higher than $10^{-3}$ S·cm$^{-1}$.$^{12}$ Liquid electrolytes usually deliver high conductivity and high switching speed$^3$, but ECDs using liquid electrolytes suffer from persistent problems, such as electrolyte leakage, flammability and chemical stability issues.

To overcome the abovementioned problems, gel polymer electrolytes (GPEs) have been developed; these GPEs generally show a much higher conductivity than solid polymer electrolytes ($> 10^{-4} \text{ vs } 10^{-8} \text{ S cm}^{-1}$)$^{4}$. GPEs refer to a family of polymer-based electrolytes that are prepared by dissolving polymer matrices into liquid electrolytes or trapping liquid electrolytes into the network of polymer matrices$^5$. The most commonly used matrices in GPEs are poly(ethylene oxide) (PEO)$^6$, poly(acrylonitrile) (PAN)$^7$, poly(vinylidene fluoride) (PVDF)$^8$, poly(vinylidene fluoride-hexafluoropropylene)
(PVDF-HFP)\textsuperscript{[9]} and polymethyl methacrylate (PMMA)\textsuperscript{[2, 8]}, additionally, the common plasticizers are propylene carbonate (PC), ethylene carbonate (EC), ethyl methyl carbonate (EMC) or their mixtures. The crystalline structure of the matrices provides the backbone of the gel, and the amorphous phase of the matrices forms the continuous phase to transport ions in the GPEs.

It is well accepted that fillers play an important role in Li\(^+\) transport, but the apparent discrepancy in electrochemical performances can partially be ascribed to the difference in electrolyte materials (polymers, salt, filler type), along with their concentration and preparation conditions. The addition of nanoparticles (such as TiO\(_2\)\textsuperscript{[10]}, CeO\(_2\)\textsuperscript{[11]}, Al\(_2\)O\(_3\)\textsuperscript{[12]}, and palygorskite\textsuperscript{[13]}) can not only improve the mechanical strength of GPEs, but also increase their conductivity by increasing the volume fraction of the amorphous phase. However, the ionic conductivity of these composite electrolytes ranges from \(10^{-4}\) to \(10^{-5}\) S cm\(^{-1}\) at ambient temperature, which is still too low for commercial applications\textsuperscript{[14]}.

Fumed SiO\(_2\) has been widely adopted as a filler to improve the conductivity and mechanical stability of GPEs, because of its branched three-dimensional structure and the flexibly-tunable surface functionalities\textsuperscript{[10]}. Currently, most studies are conducted on the development of hydrophilic fumed SiO\(_2\) as GPEs additive (with a large amount of silanol groups on the surface), because of its ionizing lithium salt and ability to increase the amorphous phase content of the polymer matrix. However, hydrophilic SiO\(_2\) with polar silanol groups tends to aggregate\textsuperscript{[15]}. Moreover, hydrophilic SiO\(_2\) presents a low compatibility with organic GPEs. Therefore, employing hydrophobic SiO\(_2\) may be a better choice for their application in GPEs due to its high dispersibility in organic matrices.

In this study, we investigate the effect of a hydrophobic fumed SiO\(_2\)/PMMA/PC/LiClO\(_4\) GPE (H-SiO\(_2\) GPE) and their applications in ECDs. It is demonstrated that hydrophobic fumed SiO\(_2\) is more efficient in increasing the ionic conductivity of electrolytes, because of the hydrophobic-hydrophobic attractions between the hydrophobic groups on the SiO\(_2\) surfaces and solvents in the GPE. The ECD assembled with H-SiO\(_2\) GPE exhibits a fast switching speed (\(t_{\text{bleaching}} = 4\) vs \(8\) s and \(t_{\text{coloring}} = 14\) vs \(16\) s). To compare, the effect of a hydrophobic fumed SiO\(_2\)/LiClO\(_4\)/PC liquid electrolyte is explored. This work demonstrates that the addition of hydrophobic fumed SiO\(_2\) in electrolytes provides great potential for use in ECDs and other energy devices.

1 Experimental section

1.1 Chemicals

Propylene carbonate (PC, 99%), lithium perchlorate (LiClO\(_4\), 99.9%), hydrophobic fumed SiO\(_2\) (Aladdin, 7-40 nm, pH=4.5), polymethyl methacrylate (PMMA, Aldrich, Mw≈1000, 000) were obtained and used.

1.2 Preparation of the liquid electrolytes and GPEs

The liquid electrolyte was prepared by dissolving 0.1 mol L\(^{-1}\) LiClO\(_4\) in 7.41 mL propylene carbonate under stirring. Afterward, 0, 20, 50, 80 and 100 mg of hydrophobic fumed SiO\(_2\) was dispersed into 10 g of liquid electrolyte with ultrasonication. This process provided hydrophobic fumed SiO\(_2\)/LiClO\(_4\)/PC liquid electrolyte with 0, 0.2wt%, 0.5wt%, 0.8wt% and 1.0wt% fumed SiO\(_2\). Hydrophobic fumed SiO\(_2\)/polymethyl methacrylate (PMMA)/PC/LiClO\(_4\) GPEs (H-SiO\(_2\) GPEs) were prepared by dissolving 1 g of PMMA (vacuum drying at 90 °C for 24 h) into 9 g of liquid electrolyte under stirring at 90 °C.

1.3 Preparation of the WO\(_3\) nanopowder

WO\(_3\) nanoparticles were synthesized using the reported hydrothermal process\textsuperscript{[16]}. In a typical experiment, 0.815 g of Na\(_2\)WO\(_4\)-2H\(_2\)O was dissolved in 10 mL of deionized water. Then the Na\(_2\)WO\(_4\) solution was acidified to a pH value of 2.0 using HCl solution at room temperature. Afterward, the solution was transferred into a Teflon-lined autoclave and heated at 180 °C for 24 h. Finally, the final products were sequentially washed with deionized water and ethanol to remove the sulfate ions and other remnants by centrifugation.

1.4 Assembly of ECDs based on different electrolytes

WO\(_3\) electrochromic films were deposited on clean ITO glasses by a wire-bar coating method, as reported in our previous work\textsuperscript{[17]}. When using the liquid electrolytes, the ECDs were sealed with 3M tape while leaving one small gap in which the LiClO\(_4\)/PC liquid electrolytes (with/without hydrophobic fumed SiO\(_2\)) were injected into the device by a syringe. Finally, the injection ports were sealed with UV curing glue. In regard to the GPEs, GPEs with/without hydrophobic fumed SiO\(_2\) were cast into WO\(_3\) electrochromic layers, and finally, these ECDs were also sealed with 3M tape.
1.5 Characterization

Viscosity measurements were determined by rotary rheometer (HAAKE MARS60) under shear rate of 0.1–100 s⁻¹ at room temperature. The morphology of WO₃ films was characterized by scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM, JEOl, JEM-2100, 200 kV). The morphologies of the gel electrolyte were characterized by FE-SEM (JEOL, JSM6700F, Tokyo). The crystal structure of the electrochromic film was required by X-ray diffraction (XRD; 3kW Bruker D8 Advance X-ray diffractometer with Cu Kα irradiation, λ=0.154 nm). The optical transmittance of the electrochromic devices was characterized by UV spectrophotometer (UH4150; Hitachi, Japan) at 633 nm. The ionic conductivity was measured by Mettler Seven compact conductivity meter. Electrochemical measurements were performed on electrochemical workstation (CHI760E, CHI Instruments, China). Electrochemical impedance spectroscopy (EIS) of the electrochromic film was recorded from 10⁻¹ to 10⁶ Hz at an amplitude of 5 mV.

2 Results and discussion

2.1 Phase characterization

The hydrophobicity of SiO₂ is suggested by the contact angle test, as presented in Fig. S1. Regardless of how the needle moves, water droplets cannot adhere to the surface of hydrophobic fumed SiO₂. Fig. 1 shows the FT-IR spectrum of the hydrophobic fumed SiO₂. The broad peaks at 3446 and 1631 cm⁻¹ are the -OH stretching and bending vibration peaks of adsorbed water, respectively. The peaks at 808 and 478 cm⁻¹ are the symmetric stretching vibrations and bending vibrations of Si-O bonds. The strong and wide absorption band at 1110 cm⁻¹ is the anti-symmetric stretching vibration peak of Si–O–Si. The peak at 979 cm⁻¹ is the stretching vibration of Si–OH, indicating the possibility for further reaction as a proton donor¹⁸. Peaks at 2976, 2927, and 2856 cm⁻¹ are the stretching vibration peaks of the -CH₃ and -CH₂– groups. Due to the existence of -CH₃, -CH₂– terminals, this fumed SiO₂ shows hydrophobic properties and good dispersibility in organic matrices, as revealed in Fig. S2. The particle size distribution of hydrophilic fumed SiO₂ shows two peaks in PC, and a strong peak in the range of 1000–10000 nm. These results indicate that hydrophilic fumed-SiO₂ can agglomerate in PC. In contrast, hydrophobic fumed-SiO₂ is mainly distributed between 100 and 1000 nm. It can be concluded that the hydrophobic fumed SiO₂ has better uniformity in PC. The scanning electron micrographs of the prepared pure GPEs and H-SiO₂ GPEs are shown in Fig. S3. H-SiO₂ is evenly distributed in the main body of the GPEs.

Fig. 1 FT-IR spectrum of hydrophobic fumed SiO₂

2.2 Effect of fumed SiO₂ on the Gel electrolyte and electrochromic devices

2.2.1 Measurements of the ionic conductivities of H-SiO₂ GPEs

A high ionic conductivity facilitates the transportation of ions into and out of an EC film to initiate a color change, which is the key indicator of an electrolyte. The ionic conductivities of these GPEs are calculated by the formula \( \sigma = L/R_bA \), where \( L \) is the thickness of the GPE electrolyte, \( A \) is the contact area between the electrolyte and the electrode, and the bulk resistance (\( R_b \)) is the intercept of the curve and the Z' axis in the AC impedances (Fig. 2(a))¹⁹. The measurement was conducted at 25 °C and 40% humidity. And the experiments were repeated three times to reduce the measuring and experimental error and obtain an average value for the final results. The conductivity of the H-SiO₂ GPE first increases and then decreases with an increasing concentration of fumed SiO₂. The GPE shows a maximum conductivity of 5.14×10⁻³ S·cm⁻¹ at 0.5 wt% concentration of fumed SiO₂ (Fig. 2(b)), which is clearly higher than the previously reported values in the literature (Table S1). The conductivity evolution of the GPEs with different SiO₂ concentrations can be explained by the trade-off between the improved dissociation of lithium perchlorate and the increase in viscosity (Fig. 2(c)). Specifically, there are a large number of methyl groups on the surface of hydrophobic SiO₂, which is the main reason for its hydrophobicity. These methyl groups can form mutual hydrophobic-hydrophobic attractions with the organic groups in organic solvents to promote the dispersion of SiO₂, thus improving the dissociation of lithium...
perchlorate and providing the GPE a high transparency. Moreover, it is noted that the polarity difference between SiO₂ with a large number of hydroxyl groups and an organic electrolyte can affect the dispersion of SiO₂ in PMMA matrices\[^{15}\], further decreasing the ionic conductivity (Table. 1). Additionally, as the viscosity continues to increase, the polar end of the molecule is gradually adsorbed on the silica surface, which halts further network formation at this site and hinders the motion of Li⁺.

2.2.2 Electrochromic performances of ECDs based on H-SiO₂ GPEs

To explore the effect of H-SiO₂ GPEs on electrochromism, the ECDs were assembled by WO₃ coated on ITO glass\[^{17}\] and using GPEs with/without hydrophobic fumed SiO₂. The specific details of WO₃ are shown in Fig. S4. The electrochemical behaviors of the ECDs were characterized by electrochemical impedance spectroscopy in the colored state (EIS, Fig. 2(d)). Each of the EIS spectra is composed of a semicircle part at high frequencies and a diagonal part at low frequencies. The semicircle part reflects the charge transfer resistance between the electrochromic film and electrolyte. The diagonal part represents the Warburg impedance that is associated with the ion diffusion process. In other words, the larger the slope of the line is, the faster the ion transfer process. Therefore, it is obvious that the resistance is low and the ion diffusion is good with H-SiO₂ GPEs.

![Fig. 2 Nyquist plots (a), ionic conductivity (b) and viscosity (c) of PMMA-based GPEs with 0, 0.2wt%, 0.5wt%, 0.8wt% and 1.0wt% fumed SiO₂. Electrochromic switching behaviors at 633 nm (e), colored state EIS (d) and CV curves (f) of ECDs contained PMMA-based GPEs with 0, 0.5wt% fumed SiO₂. Scan rate: 100mV/s](image1)

To further investigate the electrochromic performances of ECDs, as shown in Fig. 2(e). An ECD with H-SiO₂ GPEs switches faster than that without SiO₂. More precisely, the switching times are 16/14 s (coloring) and 8/4 s (bleaching) for ECDs with pure GPEs and H-SiO₂ GPEs, respectively. Compared with other similar constructions of ECDs (using WO₃, ITO glass and a gel electrolyte as electrochromic layers, substrates and ion transport layers, respectively), H-SiO₂ GPEs exhibit faster speeds than previously reported results for PVdF-HFP-based (tₐ=17 s/tₜ=28 s)\[^{20}\],

![Fig. 3 Schematic diagram of the transportation of Li⁺ ion through H-SiO₂ GPEs with three-dimensional structure](image2)
PMMA-based ($t_c=62.6\ s/h=41.2\ s$)$^{[21]}$, ionic-liquid-based ($t_c=15\ s/h=15\ s$)$^{[22]}$ and PVB-based ($t_c=16.5\ s/h=9.5\ s$)$^{[23]}$ gel electrolytes. In addition, the transmittance modulation of ECDs increases from 38.3% to 41.2%, which is higher than that reported above (41.2% vs 35%$^{[20]}$ vs 24%$^{[22]}$ vs 18%$^{[19]}$). This enhanced electrochromic performance can be attributed to the abovementioned high ionic conductivity and shear thinning behavior. The viscosity follows a linear correlation with respect to the shear rate. The viscosity as a function of shear rate for the GPE with various fumed silica contents is shown in Fig. 2(c). At a low shear rate, it exhibits a solid-like behavior with a high viscosity value due to the formation of a network structure by the induction of a siloxane linkage in the polymer matrix. At a high shear rate, because the orientation of the siloxane linkage is preferential toward being parallel to the flow direction, the viscosity decreases. Shear thinning occurs because the bonds composing the network structure are physically weak, which can be disturbed by shear$^{[24]}$, thus, the H-SiO$_2$ GPEs are proven to be physical gels with a three-dimensional network$^{[14]}$. As presented in Fig. 3, hydrophobic fumed SiO$_2$ can be attracted to the PMMA chains, forming a three-dimensional network structure, while also providing ion transport channels so that ions can transport more quickly and easily to the interface of the WO$_3$ films and electrolyte.

In addition, the CV curves of the ECDs with different GPEs are shown in Fig. 2(f). The CV curve of the SiO$_2$-free ECD has a cathode current peak at $-3.3\ V$ and an anodic current peak at $1.3\ V$. In contrast, the CV curves of the SiO$_2$ containing ECDs show cathode current peaks at $+0.37\ V$, and anodic current peaks at $-2.6\ V$. These new peaks may be attributed to different binding sites on the WO$_3$ film$^{[25]}$, indicating a better reactivity of the electrochromic WO$_3$ films at a low bias voltage. According to a previous report$^{[26]}$, the introduction of cations can decrease the reaction voltage of WO$_3$. The addition of fumed SiO$_2$ enhances the concentration of Li$^+$ near the WO$_3$ film, thus leading to better electrochromic performance.

2.3 Effect of fumed SiO$_2$ on the liquid electrolyte and electrochromic devices

For a LiClO$_4$/PC liquid electrolyte, the PC solvent has a strong solvation effect on Li$^+$ cations, but the perchlorate anions are difficult to coordinate or solvate, limiting the achievement of high conductivity in this system. The conductivity of liquid electrolytes was measured by a conductivity meter, and the results show a similar trend to that of gel electrolytes. To increase the accuracy of data, the experiment was repeated three times (Fig. 4(a)). With SiO$_2$ additives from 0 to 0.5wt%, the ionic conductivity of the liquid electrolyte increases up to a maximum of $7.58\times10^{-3}\ \text{S}\cdot\text{cm}^{-1}$, which is higher than hydrophilic fumed SiO$_2$ or other additives as fillers (no more than $7.0\times10^{-3}\ \text{S}\cdot\text{cm}^{-1}$)$^{[10,14]}$. This conductivity increase can be attributed to the reasons that have been discussed in the section on GPEs. The good dispersion of hydrophobic fumed SiO$_2$ homogenizes the electrical field$^{[27]}$. However, further increasing the SiO$_2$ concentration leads to a decrease in conductivity, possibly due to the increase in electrolyte viscosity and the aggregation of fumed SiO$_2$.

![Image](https://via.placeholder.com/150)

**Fig. 4** Ionic conductivity (a) of liquid electrolyte with 0, 0.2wt%, 0.5wt%, 0.8wt% and 1.0wt% fumed SiO$_2$, colored state Nyquist plots (b) and CV curves (c) of WO$_3$ films in liquid electrolyte with 0, 0.2wt%, 0.5wt%, 0.8wt% and 1.0wt% fumed SiO$_2$. Scan rate: 100 mV/s

The effects of the hydrophobic fumed SiO$_2$ composite electrolyte on the electrochemical behaviors of WO$_3$ films were characterized by electrochemical impedance spectroscopy in the colored state (EIS, Fig.
4(b)). As shown in Fig. 4(b), both the charge transfer resistance and ion diffusion resistance reach a minimum at a SiO₂ concentration of 0.5wt%, which is consistent with the conductivity variation. Fig. 4(c) further presents the CV curves of the WO₃ films in SiO₂ electrolytes at different concentrations. In all of CV curves, clear cathodic current peaks appear with potential sweeping from +1 V to −1 V. Moreover, the colorless WO₃ film appears blue, due to the reduction of W⁶⁺→W⁵⁺ after Li⁺ insertion. The film returns to being colorless after reverse sweeping the potential back to +1 V, suggesting the occurrence of the W⁵⁺→W⁶⁺ oxidation reaction accompanied by Li⁺ extraction. Therefore, the WO₃ film demonstrates the largest CV curve in the highly conductive electrolyte containing the addition of 0.5wt% fumed SiO₂, confirming the beneficial influence of the fumed SiO₂ additive on the electrochemical reactions of the WO₃ film.

3. Conclusion

In conclusion, the introduction of hydrophobic fumed SiO₂ into GPEs can effectively increase the conductivity from 3.99 ×10⁻³ to 5.14 ×10⁻³ S cm⁻¹, because of the attractive force of hydrophobic groups. These interactions are beneficial for increasing the compatibility between SiO₂ and GPEs, thereby promoting the dissociation of lithium perchlorate and, improving the ionic conductivity. The assembled ECDs using H-SiO₂ GPEs exhibit lower cathode interface impedances, better electrochemical behaviors, and faster switching times compared to those of the unmodified GPEs (t_bleaching = 4 vs 8 s and t_coloring = 14 vs 16 s). These observations are owing to that H-SiO₂ GPEs form a three-dimensional network structure, thereby providing an ion transport channel. Similarly, the ionic conductivity of the LiClO₄/PC/liquid electrolyte without/with hydrophobic fumed SiO₂ increases from 6.94 ×10⁻³ S cm⁻¹ (without hydrophobic fumed SiO₂) to 7.58 ×10⁻³ S cm⁻¹. This work demonstrates that the introduction of hydrophobic SiO₂ has a positive effect on electrolytes, which is an important step for their application in ECDs.

Supporting materials:
Supporting materials related to the article can be found at https://doi.org/10.15541/jim20200376.

References

[1] PATEL K J, BHATT G G, RAY J R, et al. All-inorganic solid-state electrochromic devices: a review. Journal of Solid State Electrochemistry, 2016, 21(2): 1–11.
[2] AGNIHOTRY S A, SEKHON P S S, PMMA based gel electrolyte for EC smart windows. Electrochimica Acta, 1998, 44: 3121–3126.
[3] LI H, WANG J, SHI Q, et al. Constructing three-dimensional quasi-vertical nanosheet architectures from self-assemble two-dimensional WO₃·H₂O for efficient electrochromic devices. Applied Surface Science, 2016, 380: 281–287.
[4] GROCE F, APPETECCHI G B, PERSI L, et al. Nanocomposite polymer electrolytes for lithium batteries. Nature, 1998, 394: 456.
[5] AZIZ S B, WOO T J, KADIR M F Z, et al. A conceptual review on polymer electrolytes and ion transport models. Journal of Science: Advanced Materials and Devices, 2018, 3: 1–17.
[6] TAO C, GAO M, YIN B, et al. A promising TPU/PEO blend polymer electrolyte for all-solid-state lithium ion batteries. Electrochimica Acta, 2017, 257: 31–39.
[7] JUNG H R, JU D H, LEE W J, et al. Electrosyn hydrophobic fumed silica/polycrylonitrile nanofiber-based composite electrolyte membranes. Electrochimica Acta, 2009, 54: 3630–3637.
[8] KUPPU S V, JIYARAMAN A R, GURUVIAH P K, et al. Preparation and characterization of PMMA-PVDF based polymer composite electrolyte materials for dye sensitized solar cell. Current Applied Physics, 2018, 18: 619–625.
[9] ZHAI W, ZHU H, WANG L, et al. Study of PVDF-HFP/PMMA blended micro-porous gel polymer electrolyte incorporating ionic liquid [BMIM]BF₄ for Lithium ion batteries. Electrochimica Acta, 2014, 133: 623–630.
[10] VIGNAROOBAN K, DISSANAYAKE M A K L, ALBINSSON I, et al. Effect of TiO₂ nano-filler and EC plasticizer on electrical and thermal properties of poly(ethylene oxide) (PEO) based solid polymer electrolytes. Solid State Ionics, 2014, 266: 25–28.
[11] VIJAYAKUMAR G, KARTHICK S N, SATHIYA PRIYA A R, et al. Effect of nanoscale CeO₂ on PVDF-HFP-based nanocomposite porous polymer electrolytes for Li-ion batteries. Journal of Solid State Electrochemistry, 2007, 12: 1135–1141.
[12] CROCE F, SCROSATI B, MARIOTTO G. Electrochemical and spectroscopic study of the transport properties of composite polymer electrolytes. Chem. Mater., 1992, 4: 1134–1136.
[13] YAO P, ZHU B, ZHAI H, et al. PVDF/Polygorskite Nanowire composite electrolyte for 4 V rechargeable lithium batteries with high energy density. Nano letters, 2018, 18: 6113–6120.
[14] AHMAD S, AHMAD S, AGNIHOTRY S A. Nanocomposite electrolytes with fumed silica in poly(methyl methacrylate): thermal, rheological and conductivity studies. Journal of Power Sources, 2005, 140: 151–156.
[15] JITTAICHAM M, KUSUKTHAM B. Spinning of poly(ethylene terephthalate) fiber composites incorporated with fumed silica. Silicon, 2017, 10: 575–583.
基于高电导率的疏水气相\(SiO_2\)复合凝胶电解质的高性能电致变色器件

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摘要：凝胶电解质具有化学稳定性、难燃性和易于封装等特点，其离子电导率(\(10^4 \sim 10^5 \text{ S cm}^{-1}\))阻碍了电致变色器件(EDCs)凝胶电解质的进一步发展。本研究制备了一种高电导率的疏水 \(SiO_2/PMMA/PC/LiClO_4\)凝胶聚合物电解质(\(H-SiO_2\) GPEs)并用电化学阻抗谱(EIS)、循环伏安法(CV)和计时电流法(CA)分析了GPEs的电化学行为。实验结果表明，仅引入0.5wt%的疏水性气相 \(SiO_2\), 即可使得 \(H-SiO_2\) GPEs的离子电导率达到5.14×10^{-3} \text{ S cm}^{-1}(25 \degree C)。离子电导率的增加归因于 \(SiO_2\)添加物和有机电解质之间的良好相容性和疏水-水吸力。同时，不同气相二氧化硅含量的GPEs的粘度与剪切速率的关系表现出剪切稀化行为，这表明形成三维网状结构。该结构为离子提供了传输通道，进而提高了基于 \(H-SiO_2\) GPEs电致变色器件的响应速度(\(t_{\text{on}}/t_{\text{off}} = 4 \sim 8\) s和 \(t_{\text{on}}/t_{\text{off}} = 14 \sim 16\) s)。同样，通过添加疏水性气相 \(SiO_2\)对液态电解液的探究表明：复合疏水性气相 \(SiO_2\)使得 \(LiClO_4/PC\)液态电解液的离子电导率由原来的6.94×10^{-3} \text{ S cm}^{-1}增加到7.58×10^{-3} \text{ S cm}^{-1}。疏水性气相 \(SiO_2\)作为填料对电解质的离子电导率具有一定的积极作用，\(H-SiO_2\) GPEs的研究为解决EDCs高离子电导率和易泄漏之间的矛盾提供了新思路。

关键词：凝胶电解质；电致变色；疏水性；\(SiO_2\)

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**High-conductivity Hydrophobic Fumed-SiO\textsubscript{2} Composite Gel Electrolyte for High Performance Electrochromic Devices**

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| Electrolyte | Ionic conductivity/(S·cm\textsuperscript{-1}) |
|-------------|---------------------------------------------|
| PMMA/LiClO\textsubscript{4}/hydrophobic SiO\textsubscript{2} (This work) | 5.14×10\textsuperscript{-3} |
| PMMA/LiClO\textsubscript{4}/hydrophilic SiO\textsubscript{2}\textsuperscript{[1]} | 3.8×10\textsuperscript{-3} |
| P(BMA-St)/hydrophilic SiO\textsubscript{2}\textsuperscript{[2]} | 2.15×10\textsuperscript{-3} |
| PEO/LiCF\textsubscript{3}SO\textsubscript{3}/TiO\textsubscript{2}\textsuperscript{[3]} | 1.6×10\textsuperscript{-4} |
| PVDF/LiClO\textsubscript{4}/palygorskite\textsuperscript{[4]} | 1.2×10\textsuperscript{-4} |
| PMMA/LiClO\textsubscript{4}/[Emim]BF\textsubscript{4}\textsuperscript{[5]} | 2.9×10\textsuperscript{-3} |
| PVDF/HFP/LiCF\textsubscript{3}SO\textsubscript{3}/ZrO\textsubscript{2}\textsuperscript{[7]} | 4.0×10\textsuperscript{-5} |
| PAN/LiClO\textsubscript{4}/Li\textsubscript{0.33}La\textsubscript{0.557}TiO\textsubscript{3}\textsuperscript{[8]} | 6.05×10\textsuperscript{-5} |

**Fig. S1** The static water contact angle (CA) of hydrophobic fumed SiO\textsubscript{2}

**Fig. S2** Particle size of hydrophobic fumed silica (a) and hydrophilic fumed silica (b) in PC

**Table S1** Ion conductivity of gel electrolytes from the literature

**Fig. S3** SEM images of pure GPEs (a) and 0.5wt% H-SiO\textsubscript{2} GPEs (b)

**Fig. S4** XRD patterns of the as-prepared WO\textsubscript{3} (a), SEM image of WO\textsubscript{3} films coated on ITO substrates (b), TEM images of WO\textsubscript{3} dispersion (c) and typical nanorod (d) with high magnification.
References

[1] AHMAD S, AHMAD S, AGNIHOTRY S A. Nanocomposite electrolytes with fumed silica in poly(methyl methacrylate): thermal, rheological and conductivity studies. Journal of Power Sources, 2005, 140: 151–156.

[2] LIAO Y H, RAO M M, LI W S, et al. Fumed silica-doped poly(butyl methacrylate-styrene)-based gel polymer electrolyte for lithium ion battery. Journal of Membrane Science, 2010, 352: 95–99.

[3] VIGNAROOBAN K, DISSANAYAKE M A K L, ALBINSSON I, et al. Effect of TiO₂ nano-filler and EC plasticizer on electrical and thermal properties of poly(ethylene oxide) (PEO) based solid polymer electrolytes. Solid State Ionics, 2014, 266: 25–28.

[4] YAO P, ZHU B, ZHAI H, et al. PVDF/palygorskite nanowire composite electrolyte for 4 V rechargeable lithium batteries with high energy density. Nano letters, 2018, 18: 6113–6120.

[5] TANG Q, LI H, YUE Y, et al. 1-Ethyl-3-methylimidazolium tetrafluoroborate-doped high ionic conductivity gel electrolytes with reduced anodic reaction potentials for electrochromic devices. Materials & Design, 2017, 118: 279–285.

[6] ZHANG F, DONG G, LIU J, et al. Polyvinyl butyral-based gel polymer electrolyte films for solid-state laminated electrochromic devices. Ionics, 2017, 23: 1879–1888.

[7] PUGUAN J M C, CHINNAPPAN A, APPIAH-NTIAMOAH R, et al. Enhanced Ionic conductivity and optical transmissivity of functionalized ZrO₂/PVdF-HFP hybrid electrolyte for energy efficient windows. Solar Energy Materials and Solar Cells, 2015, 137: 265–273.

[8] LIU W, LEE S W, LIN D. Enhancing ionic conductivity in composite polymer electrolytes with well-aligned ceramic nanowires. Nature Energy, 2017, 2(5): 17035.