ELSEVIER

Full paper

Contents lists available at ScienceDirect

Nano Energy



journal homepage: http://www.elsevier.com/locate/nanoen

Nanocomposite with fast Li⁺ conducting percolation network: Solid polymer electrolyte with Li⁺ non-conducting filler

Xin Ao^a, Xiaotao Wang^a, Jiewen Tan^b, Shaolong Zhang^a, Chenliang Su^a, Lei Dong^c, Mingxue Tang^d, Zhongchang Wang^e, Bingbing Tian^{a,*}, Haihui Wang^{b,*}

a SZU-NUS Collaborative Innovation Center for Optoelectronic Science & Technology, International Collaborative Laboratory of 2D Materials for Optoelectronics Science

and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, China

^c School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

^d Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China

^e Department of Quantum and Energy Materials, International Iberian Nanotechnology Laboratory (INL), Braga 4715-330, Portugal

ARTICLE INFO

Keywords: Solid polymer electrolytes Li⁺ conductivity Oxygen vacancies CeO₂ nanowires Li⁺ fast conducting percolation network

ABSTRACT

Solid polymer electrolytes (SPEs) have attracted considerable research interest because they are expected to solve the safety problems caused by the liquid electrolytes. However, the low ionic conductivity limits their practical applications. Constructing Li⁺ fast conducting network in SPEs with Li⁺ highly conducting ceramic fillers following the mixed matrix membrane concept have shown their limits in raising the Li⁺ conductivity. Herein, a new strategy using Li⁺ non-conducting fillers like CeO₂ nanowires, is proposed to construct a Li⁺ fast conducting network through SPEs. CeO₂ nanowires can dissociate LiTFSI, which results in a high Li⁺ conductivity through the SPEs near to the fiber surface. This experimental finding is confirmed by analytics (FT-IR, Raman and NMR) and theoretical calculations (DFT-MD and COHP). As a result, the network of interwoven CeO₂ nanowires helps form a continuous Li⁺ fast conducting percolation network through the SPEs with 10 wt% CeO₂ nanowires is greatly improved $(1.1 \times 10^{-3} \text{ s cm}^{-1} \text{ at 60 °C})$. The Li symmetric cells with this composite electrolyte exhibit good cyclic stability (without short circuiting after 2000 h), and the all-solid-state LiFePO₄/Li cells present a superior cycling performance (remained 140 mA h g⁻¹ after 100 cycles at 1 C).

1. Introduction

Lithium-ion batteries (LIBs) are currently developed to meet the increasing energy demands ranging from portable devices to electric vehicles and large-scale energy storage systems [1,2]. However, traditional commercial LIBs with liquid organic electrolytes have severe safety risks, such as electrolyte leakage, flammability, or even explosion [3]. Solid-state electrolytes (SSEs) have attracted much research interest because they are expected to solve the security issue resulting from the use of liquid electrolytes [4–8]. Until now, two general types of Li-ion solid electrolytes have been investigated: ceramic electrolytes and solid polymer electrolytes (SPEs) [5,9]. A large number of ceramic electrolytes have been widely studied, such as garnet oxides, [10–12] NASICON-type phosphates, [13–15] (anti)perovskite type, [16–18] thio-LISICON [13,19] and sulfide-based ceramics [20,21]. In general,

ceramic Li-ion electrolytes have a relatively high ionic conductivity and lithium transfer number as well as good mechanical, chemical and thermal stability, but the high interfacial impedance with the electrodes and the difficult fabrication process impedes their practical application in all-solid-state lithium metal batteries (LMBs) [9].

In contrast to ceramic electrolytes, SPEs have better flexibility, lower interfacial resistance and manufacturing cost, and easier stacking and sealing, which is beneficial for the manufacture and indicates a promising future for all-solid-state batteries. However, the greatest challenge for the practical application of SPEs mainly lies in its poor ionic conductivity [5–7], for example, PEO-based SPEs have only an ionic conductivity of approximately 10^{-7} – 10^{-6} S cm⁻¹ at room temperature [22]. Since Li-ion migration mainly occurs in an amorphous region of PEO [23], dispersing inorganic nanoparticles, including TiO₂ [24–26], Al₂O₃ [27,28], SiO₂[29], ZrO₂[30], Li_{1+x}Al_yGe_{2-y}(PO₄)₃ (LAGP) [31] and

* Corresponding authors. *E-mail addresses:* tianbb2011@szu.edu.cn (B. Tian), hhwang@scut.edu.cn (H. Wang).

https://doi.org/10.1016/j.nanoen.2020.105475

Received 30 July 2020; Received in revised form 25 September 2020; Accepted 9 October 2020 Available online 12 October 2020 2211-2855/© 2020 Elsevier Ltd. All rights reserved.

^b School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

Li₇La₃Zr₂O₁₂ (LLZO) [32,33] etc., within the polymer matrix has been proven to be an effective approach to prevent crystallization thus improving the ionic conductivity. Additionally, experimental research has shown that surface groups such as Lewis acid sites of the inorganic nanofillers are able to dissociate Li salts since they interact with the anions of salts thus liberating free Li⁺ which improves the ionic conductivity [24,34–36]. Filler materials with oxygen vacancies have been developed to improve the ionic conductivity of SPEs due to the positively charged oxygen vacancies that could serve as Lewis acid sites in the composite solid polymer electrolytes (CSPEs) [37–39]. Lately, Goodenough and coworkers confirmed that some inorganic oxides with oxygen vacancies could dissociate Li salt and release free Li⁺ by means of Li solid-state nuclear magnetic resonance (NMR) measurements [40].

The construction of Li⁺ fast conducting network in SPEs is increasingly being recognized as an effectively strategy to further enhance the Li⁺ conductivity. Li⁺ conducting ceramic nanowire as fillers are primarily considered to construct Li⁺ conducting network in SPEs. The Li⁺ conducting ceramic nanowires, including Li_{6.4}La₃Zr₂Al_{0.2}O₁₂ (LLZAO) [41,42], Li_{0.33}La_{0.557}TiO₃ (LLTO) [43–46], and Li₇La₃Zr₂O₁₂ (LLZO) [47], are used to form fast Li⁺ conducting networks through the SPEs to improve their ionic conductivity. However, Li⁺ conducting materials are expensive and difficult to fabricate. On the other hand, a large number of cheap and easy-fabricated Li⁺ non-conducting nanofillers are available. Among them, the cerium dioxide (CeO₂) is a recently emerging filler [39,40], which possess abundant oxygen vacancies on the surface, and is expected to dissociate Li salts and release free Li⁺ ions near the surface [48].

In this work, we use a Li⁺ non-conducting filler, CeO₂ nanowires, to construct Li⁺ fast conducting percolation network through SPEs to further enhance the Li⁺ conductivity. Fourier transform infrared spectroscopy (FT-IR), Raman spectra, solid-state NMR, density functional theory based molecular dynamics (DFT-MD) simulation and crystal orbital Hamilton population (COHP) analyzes confirmed that CeO₂ with surface oxygen vacancies can dissociate Li-bis (trifluoromethanesulfonyl)imide (LiTFSI) and release free Li⁺ ions

(Fig. 1a). Thus, the free Li^+ enriched polymer near the surface of CeO₂ can be regarded as Li⁺ fast conducting pathway, while the polymer far from CeO₂ surface is Li⁺ slow conducting (Fig. 1b–d). In the CSPEs with CeO₂ nanowires (denoted as CSPE-xNW, x% is the mass content of CeO₂ nanowires), the network of interwoven CeO2 nanowires helps to form a continuous Li⁺ fast conducting percolation network in SPEs (Fig. 1b). In the CSPEs with CeO₂ nanoparticles (denoted as CSPE-xNP, x% is the mass content of CeO_2 nanoparticles), there is a high Li^+ conductivity around the filler but no long-range fast conducting pathways exist (Fig. 1c). In contrast, in Fig. 1d only Li⁺ slow conducting pathways exist in the filler-free SPEs (SPE-blank). Consequently, the ionic conductivity of the CeO₂ nanowire-modified SPEs is greatly improved, which is comparable with or even better than that of other Li⁺-conductive nanowire-modified SPEs [44,47,49]. Moreover, the continuous network formed by CeO₂ nanowires strengthens the mechanical properties of the CSPEs and inhibits the growth of lithium dendrites. Benefiting from these merits, Li symmetric cells with these CSPEs exhibit good cyclic stability (without short circuiting even after 2000 h), and the all-solidstate LiFePO₄/Li cells present a superior cycling performance (remained 140 mA h g⁻¹ at 1 C after 100 cycles at 60 °C).

2. Results and discussion

The macroscopic morphology of the as prepared CeO₂ nanowires (Fig. S1) is extremely fluffy, with a network structure composed of interconnected nanowires (Fig. 2a). The nanowires are very uniform (Fig. S2) with a diameter of less than 10 nm and an aspect ratio greater than 100 (Fig. 2b, c). The nanowires are further characterized by the high-resolution TEM (HRTEM, Fig. 2d), which shows visible lattice fringes with p-spacing values of 0.313 and 0.277 nm, corresponding to the theoretical (111) and (200) lattice planes of CeO₂, respectively. The fast Fourier transform (FFT) image (inset of Fig. 2d) also demonstrates the crystalline nature of the CeO₂ nanowires, showing p-spacing values of CeO₂ with the lattice planes (111) (0.312 nm) and (200) (0.271 nm). The photographs and SEM images of the CSPE-10NW and SPE-blank are



Fig. 1. Schematic illustration of the composite SPE with CeO₂ nanowires in comparison with the SPE with CeO₂ nanoparticles and filler free-SPE.



Fig. 2. (a) SEM image; (b), (c) TEM images, (d) high resolution TEM image and the corresponding FFT pattern (inset) of CeO₂ nanowires; (e) HAADF-STEM image and corresponding elemental mappings of CSPE-10NW; (f) TEM image, diameter distribution (inset) and (g) high resolution TEM image of the CeO₂ nanoparticles; (h) XRD patterns, (i) XPS spectra and (j) Zeta potential of CeO₂ nanowires and nanoparticles.

shown in Fig. S3. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and corresponding elemental mappings of the CSPE-10NW indicate that the CeO₂ nanowires are still interwoven forming a network in the CSPE (Fig. 2e). TEM and HRTEM images of the as-prepared CeO₂ nanoparticles are shown in Fig. 2f. g. The size of the nanoparticles is ~ 10 nm, which is similar to the diameter of the CeO₂ nanowires; in addition, the inter-planar spacing of the order stripe is 0.311 nm, which is in consistent with the (111) lattice plane of CeO₂. The X-ray diffraction (XRD) patterns of the CeO₂ nanoparticles and nanowires (Fig. 2h) demonstrate that the asprepared products are CeO₂ (JCPDS card no. 75-0120), in agreement with the above HRTEM results. The electron paramagnetic resonance (EPR) spectrum of CeO₂ nanowires (Fig. S4) exhibits an obvious symmetrical signal, which is originated from the unpaired electron trapping at the oxygen vacancies [50,51]. Fig. 2i shows the XPS Ce(3d) spectra of the CeO₂ nanoparticles and nanowires in the binding energy range of 875–925 eV, the peaks positions and integrated areas of Ce^{3+} and Ce^{4+} ions are also listed in Tables S1 and S2. The Ce³⁺ concentration and corresponding oxygen vacancy concentration of CeO2 nanoparticles are calculated to be 35.7% and 8.9%, similarly to those of CeO_2 nanowires which are calculated to be 36.1% and 9.1%. Fig. 2j gives the Zeta potential of the CeO_2 nanoparticles and nanowires with a pH of 7 in distilled water. The positive Zeta potential of both CeO2 nanoparticles (+12.1 mV) and nanowires (+13.0 mV) indicates a Lewis acidity, owing

to the oxygen vacancies as Lewis acid sites. Moreover, the nitrogen adsorption isotherm results (Figs. S5 and S6) reveal that the specific surface area of as-synthesized nanoparticles and nanowires are 87.9 and 99.9 m² g⁻¹, respectively. The concentration of oxygen vacancy, Zeta potential and specific surface area data reveal similar surface properties of CeO₂ nanowires and nanoparticles.

The XRD patterns of the SPE-blank, CSPE-10NP and CSPE-10NW (Fig. 3a) clearly reveal that the characteristic peaks of PEO at 19° and 23° become weaker in CSPE-10NP and CSPE-10NW [52,53], which implies their lower crystallinity. The DSC curves of these three polymer electrolytes (Fig. 3b) indicate that the glass transition temperature (T_g) of CSPE-10NW (-41.6 °C) and CSPE-10NP (-41.2 °C) are lower than that of SPE-blank (-35.8 °C). The decrease of the T_g of the CSPEs with fillers indicates the lower crystalline state of PEO after the addition of CeO₂ nanowires and nanoparticles. Remarkably, the difference in the crystallinity reduction between CSPE-10NP and CSPE-10NW is quite similar. Fig. 3c shows the FT-IR spectra for CSPE-10NW, SPE-blank, PEO, LiTFSI, and CeO₂ nanowires in the 1500–1000 cm⁻¹ region. After the addition of CeO2 nanowires into the SPE, the peaks at 1335 and 1204 cm⁻¹ attenuate in intensity and show fewer splits, which implies less TFSI⁻ aggregates and more "free TFSI⁻" in CSPE-10NW [53,54]. The Raman spectra of SPE-blank and CSPE-10NW are shown in the frequency range of 732–762 cm^{-1} (Fig. 3d). The band at 740–744 cm^{-1} (P1) is attributed to the response of the free uncoordinated TFSI,



Fig. 3. (a) XRD patterns and (b) DSC curves of SPE-blank, CSPE-10NP and CSPE-10NW; (c) Fourier transform infrared (FTIR) spectra of CSPE-10NW, SPE-blank, PEO, LiTFSI, and CeO₂ nanowires; (d) Raman spectra of CSPE-10NW and SPE-blank, fitted with the P1 and P2 bands; (e) Solid-state ⁶Li NMR spectra for CSPE-10NW and SPE-blank, (f) Chronoamperometry curves of Li/CSPE-10NW/Li cells at a potential of 10 mV at 60 °C, (inset) EIS spectra of the same cell before and after polarization.

whereas ion clusters (TFSI⁻ coordinated with Li⁺) correspond to the band at 747–750 cm⁻¹ (P2) [54–56]. If we assume the scattering cross-sections of the free uncoordinated TFSI⁻ and the ion cluster to be similar, the percentage of "free TFSI⁻" can be calculated as follows [56]:

$$[free \ TFSI^{-}] = \frac{A(P1)}{A(P1 + P2)} \times 100\%$$
(1)

where A(P1) is the integrated intensity of the P1 band and A(P2) is that of the P2 band. The percentage of free TFSI⁻ in SPE-blank (Fig. 3d-I) is 39.6%, indicating the abundant existence of ion clusters. In CSPE-10NW (Fig. 3d-II), the P2 band is greatly reduced and the percentage of free TFSI⁻ reaches 77.0%, signifying the better dissociation of ion clusters. The solid-state ⁶Li NMR spectra for LiTFSI in CSPE-10NW and SPE-blank (Fig. 3e) show that the signal is shifted downfield in the CSPE-10NW (-0.01 ppm) compared to SPE-blank (-0.20 ppm). This downfield shift is indicative of reduced electron density around the Li atom, suggesting looser coordination with the donating nitrogen electrons in the TFSI⁻, [57,58] which is possibly caused by the higher dissociation degree of LiTFSI upon inducing CeO2 nanowires. This is in good line with the change of full width at half maximum (FWHM) from SPE-blank (0.18) to CSPE-10NW (0.22) in ⁷Li NMR spectra as demonstrated in Fig. S7. The lithium transference number (t^+) of CSPE-10NW (0.47, Fig. 3f) and CSPE-10NP (0.40, Fig. S8) are almost 2 times higher than that of SPE-blank (0.19, Fig. S9), which demonstrates increased concentration of free Li⁺.

Temperature-dependent ionic conductivity curves (Fig. 4a) reveal that the ionic conductivity improves with increasing temperature (from 30 °C to 80 °C). A content of 10 wt% CeO₂ nanowires was found to be optimal, and higher filler concentrations (12 wt% and 15 wt%) result in a decrease of the ionic conductivity in the CSPEs (Fig. S10). The reduction of the ionic conductivity with further increased concentrations of CeO₂ nanowires filler may be attributed to the agglomeration of

nanowires and a decrease of the free-volume in the polymer [52,59]. The electrochemical impedance spectroscopy (EIS) spectra of CSPE-10NW at different temperatures (Fig. S11) show that the value of the impedance gradually decreases with increasing temperature. As shown in Fig. 4a and b, CSPE-10NW reaches a superior ionic conductivity of 1.1×10^{-3} S cm⁻¹ at 60 °C, which is well above that of SPE-blank $(2.8 \times 10^{-4} \text{ S cm}^{-1})$ and almost 2 times higher than that of CSPE-10NP (5.9 \times 10 $^{-4}$ S cm $^{-1}$) at 60 °C. The improvement of Li $^+$ conductivity is ascribed to the following two reasons: first, the reduction of the crystallinity of the PEO matrix; and second, the formation of fast Li^+ conducting pathways near the surface of the CeO₂ nanofillers which cause the Li salt to dissociate and release free Li⁺. The traditional Li⁺ conducting pathway without the dissociation function of CeO₂ is regarded as Li⁺ slow conducting pathway. The crystallinity of PEO matrix in CSPE-10NW and CSPE-10NP is similar. The much higher ionic conductivity of CSPE-10NW in comparison with CSPE-10NP clearly illustrates that the network of interwoven CeO₂ nanowires forms a percolating system. In the polymer matrix nearby the nanowires, a continuous Li⁺ fast conducting percolation network through the SPE is formed. In CSPE-10NP, the fast Li⁺ conducting pathways also exist near the surface of the CeO₂ nanoparticles but cannot form a percolation network. Therefore, the CSPE-10NP contains both fast and slow Li⁺ conducting pathways simultaneously, but no long-range fast conductivity pathways. By contrast, only Li⁺ slow conducting pathways exist in SPE-blank, which are responsible for its poor ionic conductivity. Noteworthy, the ionic conductivity of CSPE-10NW is comparable with or even better than that of other Li⁺ conductive frameworks modified SPEs (Table S3), which suggests the validity of the Li⁺ fast conducting percolation network constructed by Li+-non-conducting CeO2 nanowires.

The electrochemical operating windows measured by linear sweep voltammetry (LSV) are shown in Fig. 4c. Both CSPE-10NW and CSPE-10NP exhibit a steady platform at approximately 5.1 V, which is much



Fig. 4. (a) Temperature dependence of the ionic conductivities of nanocomposites with different content of nanowires from 30 °C to 80 °C. (b) Temperature dependence of the ionic conductivities and (c) linear sweep voltammetry of the SPE-blank, CSPE-10NP and CSPE-10NW samples. (d) Voltage profiles of the continued lithium plating/stripping cycling of Li/SPE-blank/Li, Li/CSPE-10NP/Li and Li/CSPE-10NW/Li symmetric cells with a current density of 0.25 mA cm⁻² at 60 °C. (e) EIS spectra of Li symmetric cells using the SPE-blank, CSPE-10NP and CSPE-10NW electrolytes at 60 °C before electrochemical cycling test. Selected voltage profiles of (f) the 0–5th, (g) 585th-590th, (h) 1441th-1446th.

higher than that of SPE-blank (~ 4.0 V). The stress-strain curves of the SPE-blank, CSPE-10NP and CSPE-10NW electrolytes are shown in Fig. S12, and the calculated Young's modulus of CSPE-10NW (33.0 MPa) is much larger than those of the CSPE-10NP (6.97 MPa) and SPE-blank (1.87 MPa) samples. The interlinked networks of nanowires and strong cross-linking interactions between polymer chains and the nanowires can also improve the mechanical properties of the CSPE-10NW electrolytes. TGA analyzes of the above three types of electrolytes were conducted to evaluate their thermal stability (Fig. S13). The galvanostatic cycling performances of Li/SPE/Li symmetric cells are tested at 0.25 mA cm⁻² for 1 h each cycle at 60 °C (Fig. 4d). As shown, the cell with CSPE-10NW has a low initial overpotential of 50 mV; subsequently, the overpotential gradually decreases to 45 mV, and then shows a slow and sustained growth, which is less than 56 mV even after 2000 h. In contrast, the cells with SPE-blank and CSPE-10NP have a higher initial overpotential (78 and 60 mV, respectively) and exhibit sudden short circuits after 587 (Fig. 4g) and 1443 (Fig. 4h) hours due to internal short circuits by lithium dendrites. EIS spectra of symmetric cells with above three types of SPEs at 60 °C before cycling are shown in Fig. 4e. The value of charge transfer resistance (Rct, semicircle in the EIS spectra) of the cells with CSPE-10NW and CSPE-10NP are much lower than that of the cell with SPE-blank, indicating that the addition of CeO_2 nanofillers in the CSPEs is beneficial for the transportation of Li⁺. EIS spectra of Li/CSPE-10NW/Li symmetric cell after different cycles are shown in Fig. S14. After approximately 500 h of cycling, massive irregular lithium dendrites could be observed on the Li anode of the symmetric cell using SPE-blank (Fig. S15). In sharp contrast, the Li anode of the symmetric cell using CSPE-10NW has a relatively uniform and smooth surface with only a few lithium dendrites (Fig. S16), which is ascribed to the high ionic conductivity, high Li⁺ transference number and superior mechanical property of the CSPE-10NW.

All-solid-state LiFePO₄/Li (LFP/Li) batteries using SPE-blank, CSPE-10NP and CSPE-10NW electrolytes were assembled to verify their stability and electrochemical performances in solid-state batteries (Fig. 5). The LFP/CSPE-10NW/Li cell delivers a specific capacity of 164 mA h g⁻¹ after 100 cycles with a capacity retention of 98% at 0.1 C under 60 °C (Fig. 5a), approaching the theoretical capacity (172 mA h g⁻¹) of LiFePO₄ cathode. The cell can still work even after 280 cycles with a capacity retention of 91% (Fig. S18), indicating good cycling stability of the composite electrolyte. In contrast, the LFP/SPE-



Fig. 5. Cycling performances of the all-solid-state LFP/Li batteries (a) with SPE-blank, CSPE-10NP and CSPE-10NW at 0.1 C, (b) with CSPE-10NW at 0.2, 0.5 and 1 C under 60 °C and (c) with SPE-blank and CSPE-10NW at 0.1 C under 30 °C. Charge-discharge voltage profiles of the all-solid-state LFP/Li batteries with CSPE-10NW (d) at the 1st, 10th, 30th, 100th cycles at 0.1 C under 60 °C, (e) at the 10th cycle at 0.2, 0.5 and 1 C under 60 °C and (f) at the 1st, 10th, 30th, 100th cycles at 0.1 C under 30 °C.

blank/Li cell has a low initial specific capacity with poor cycling stability and short circuits after 45 cycles. The charge-discharge curves of the LFP/CSPE-10NW/Li cell at 0.1 C under 60 °C exhibit a small voltage polarization of 0.06 V even after 100 cycles (Fig. 5d). In comparison, the cell with the SPE-blank has a relatively low overpotential in the beginning (0.07 V), but rapidly increased to 0.23 V after 40 cycles (Fig. S19). The LFP/CSPE-10NW/Li batteries exhibit good cycling performances at different current rates (Fig. 5b), maintaining discharge capacities of 158, 150 and 140 mA h g $^{-1}$ at 0.2, 0.5 and 1 C, respectively, after 100 cycles. The 10th charge-discharge curves of the cells with CSPE-10NW at different current rates (Fig. 5e) show only a slight increase of the overpotential (0.07, 0.09 and 0.11 V at 0.2, 0.5 and 1 C, respectively). The LFP/Li cell using CSPE-10NW also exhibits good cycling stability even at 30 °C (Figs. 5c and S20), with a specific capacity of 158 mA h g⁻¹ after 100 cycles and 150 mA h g⁻¹ even after 450 cycles at 0.1 C. In contrast, the LFP/Li cell using SPE-blank hardly works at 30 °C. The overpotential indicated by the charge-discharge curves of the cells using CSPE-10NW (Fig. 5f) and SPE-blank (Fig. S21) are ~ 0.16 and \sim 0.31 V at 0.1 C under 30 °C. The above mentioned favorable comprehensive performance of CSPE-10NW ensure that the all-solidstate batteries using this composite electrolyte possess excellent electrochemical performance in terms of capacity, cycle life and rate capability.

The binding energy of Li⁺ with TFSI⁻ in LiTFSI can be predicted in DFT calculations. Chen et. al. [39] have been confirmed the dissociation process of LiTFSI salt in a thermodynamic method. Here we performed a dynamic method, DFT-based MD simulations to further evaluate the molecular interaction between the surface of CeO₂ and LiTFSI. Fig. 6a shows the molecular structure model including the Li salt (LiTFSI) and CeO₂ (with oxygen vacancy in the surface) in the initial (0 ps) and after 2 ps MD simulation. The distance (D) evolution with increasing time between Li and N (Fig. 6b) shows that the two atoms oscillate about an equilibrium position with a gradually increasing amplitude. Interestingly, after a critical point the distance increases sharply. Noteworthy that the Li–N distance increases from initially 2.05 to 3.98 Å after 2 ps MD simulation, which is much longer than an ordinary bond length. The dynamic change process of the LiTFSI can be seen in the video

(Supporting Information). As shown in the video, the TFSI⁻ ion performs a distinct rotation: In the initial stage, the oxygen atoms in TFSI- are away from the CeO₂ surface, but they gradually rotate to the position near the surface of CeO_2 with increasing time (Fig. 6a, b), which is in accordance with previous reports that positively charged oxygen vacancy can attract and interact with TFSI-. [37,38] Crystal orbital Hamilton population (COHP) is proved in retrieving the chemical bonding information [60,61]. We performed the COHP method to analyze the nature of the Li-N bond in an isolated LiTFSI molecule and of the Li–N bond in a LiTFSI near the surface of CeO₂ after 0 ps and 2 ps MD simulation. In the COHP diagram, the resulting plane-wave-COHP-(E) plots draws negative (bonding) contributions to the upper part and positive (antibonding) to the lower part. No obvious antibonding peak exists in the COHP diagram of Li-N bond in isolated LiTFSI molecule (Fig. S23). By contrast, an obvious antibonding peak presents in the COHP diagram of Li-N bond in LiTFSI in the initial state of MD simulation (vellow line, Fig. 6c), prefiguring instability of the Li-N bond when LiTFSI is in the vicinity of CeO₂ surface (with oxygen vacancy). The integrated-COHP of Li-N bond in LiTFSI (from -10 to 0 eV) at 0 ps is 0.193, while that at 2 ps is only - 0.012, indicating a strong bonding ability (bonding) at 0 ps and an extremely weak interaction (nonbonding) at 2 ps between the Li and N atoms. The DFT-based MD simulations and COHP analyses indicate that CeO₂ with oxygen vacancy will help to dissociate LiTFSI and release free Li⁺, which agrees with the FTIR, Raman, solid-state NMR and the lithium transference number measurements. Therefore, as expected, an area enriched with free Li⁺ exists on the CeO2 surface within the CSPE forming fast conducting pathways.

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2020.105475.

3. Conclusion

In summary, by bringing Li^+ -non-conducting fillers, interlinked CeO₂ nanowires or CeO₂ nanoparticles with surface oxygen vacancies into a solid polymer electrolyte (SPE), increased Li^+ conductivity in the interface is observed. The surface oxygen vacancies have the function to



Fig. 6. (a) Molecular structure of the LiTFSI and CeO₂ surface before DFT-MD simulation (0 ps) and after simulation (2 ps). (b) Calculated atomic distance between Li and N as a function of the simulation time based on DFT-MD simulations. (c) COHP analysis for the interactions between Li and N of LiTFSI at 0 and 2 ps.

catalytically dissociate Li-bis(trifluoromethanesulfonyl)imide (LiTFSI) thus creating in the polymer matrix nearby the nanowires a continuous Li⁺ fast conducting percolation network through the SPEs. As a result, the composite SPE with 10 wt% CeO₂ nanowires has an improved Li⁺ ionic conductivity (1.1×10^{-3} S cm⁻¹ at 60 °C). The Li symmetric cells with the composite electrolyte exhibit good cyclic stability (without short circuit after 2000 h) and the all-solid-state LFP/Li cells also possess a superior cycling performance (remained 140 mA h g⁻¹ at 1 C after 100 cycles) at 60 °C. The present work provides a new strategy of constructing Li⁺ fast conducting percolation network through SPEs by filling easy-fabricated and low-cost Li⁺-non-conducting nanofillers, which will break a new path for the design of high-performance solid polymer electrolytes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by Guangdong Natural Science Foundation (2019A1515010675), the Science and Technology Planning Project of Shenzhen of China (Grant Nos. JCYJ20180305125106329, JCYJ20190808142209376 and ZDSYS201707271014468), the Shenzhen Peacock Plan (Grant Nos. 827-000273, KQJSCX20180328094001794, and KQTD2016053112042971). Prof. C. Su acknowledges the support from the Guangdong Special Support Program. The authors thank Dr. Nan Jian from the Electron Microscope Center of Shenzhen University for his help in HRTEM measurement.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2020.105475.

References

- G. Zubi, R. Dufo-López, M. Carvalho, G. Pasaoglu, The lithium-ion battery: state of the art and future perspectives, Renew. Sustain. Energy Rev. 89 (2018) 292–308.
- [2] B. Dunn, H. Kamath, J.-M. Tarascon, Electrical energy storage for the grid: a battery of choices. Science 334 (2011) 928–935.
- [3] J. Zhu, T. Wierzbicki, W. Li, A review of safety-focused mechanical modeling of commercial lithium-ion batteries, J. Power Sources 378 (2018) 153–168.
- [4] F. Zheng, M. Kotobuki, S. Song, M.O. Lai, L. Lu, Review on solid electrolytes for allsolid-state lithium-ion batteries, J. Power Sources 389 (2018) 198–213.
- [5] S.-J. Tan, X.-X. Zeng, Q. Ma, X.-W. Wu, Y.-G. Guo, Recent advancements in polymer-based composite electrolytes for rechargeable lithium batteries, Electrochem. Energy Rev. 1 (2018) 113–138.
- [6] C. Sun, J. Liu, Y. Gong, D.P. Wilkinson, J. Zhang, Recent advances in all-solid-state rechargeable lithium batteries, Nano Energy 33 (2017) 363–386.

- [7] A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes, Nat. Rev. Mater. 2 (2017) 16103.
- [8] S. Xin, Y. You, S. Wang, H.-C. Gao, Y.-X. Yin, Y.-G. Guo, Solid-state lithium metal batteries promoted by nanotechnology: progress and prospects, ACS Energy Lett. 2 (2017) 1385–1394.
- [9] L. Fan, S. Wei, S. Li, Q. Li, Y. Lu, Recent progress of the solid-state electrolytes for high-energy metal-based batteries, Adv. Energy Mater. 8 (2018), 1702657.
- [10] V. Thangadurai, S. Narayanan, D. Pinzaru, Garnet-type solid-state fast Li ion conductors for Li batteries: critical review, Chem. Soc. Rev. 43 (2014) 4714–4727.
 [11] R. Murugan, V. Thangadurai, W. Weppner, Fast lithium ion conduction in garnet-
- type Li₇La₃Zr₂O₁₂, Angew. Chem. Int. Ed. 46 (2007) 7778–7781.
 [12] S. Ramakumar, C. Deviannapoorani, L. Dhivya, L.S. Shankar, R. Murugan, Lithium garnets: synthesis, structure, Li⁺ conductivity, Li⁺ dynamics and applications, Prog. Mater. Sci. 88 (2017) 325–411.
- [13] J.C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S.F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, Inorganic solid-state electrolytes for lithium batteries: mechanisms and properties governing ion conduction, Chem. Rev. 116 (2016) 140–162.
- [14] H. Kitaura, H. Zhou, Electrochemical performance and reaction mechanism of allsolid-state lithium-air batteries composed of lithium, Li_{1+x}Al_yGe_{2-y}(PO₄)₃ solid electrolyte and carbon nanotube air electrode, Energy Environ. Sci. 5 (2012) 9077–9084.
- [15] Y. Li, W. Zhou, X. Chen, X. Lü, Z. Cui, S. Xin, L. Xue, Q. Jia, J.B. Goodenough, Mastering the interface for advanced all-solid-state lithium rechargeable batteries, Proc. Natl. Acad. Sci. 113 (2016) 13313–13317.
- [16] C. Ma, K. Chen, C. Liang, C.-W. Nan, R. Ishikawa, K. More, M. Chi, Atomic-scale origin of the large grain-boundary resistance in perovskite Li-ion-conducting solid electrolytes, Energy Environ. Sci. 7 (2014) 1638–1642.
- [17] Z. Jiang, H. Xie, S. Wang, X. Song, X. Yao, H. Wang, Perovskite membranes with vertically aligned microchannels for all-solid-state lithium batteries, Adv. Energy Mater. 8 (2018), 1801433.
- [18] Z. Jiang, S. Wang, X. Chen, W. Yang, X. Yao, X. Hu, Q. Han, H. Wang, Tape-casting Li_{0.34}La_{0.56}TiO₃ ceramic electrolyte films permit high energy density of lithiummetal batteries, Adv. Mater. 32 (2020), 1906221.
- [19] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, A lithium superionic conductor, Nat. Mater. 10 (2011) 682–686.
- [20] Z. Liu, W. Fu, E.A. Payzant, X. Yu, Z. Wu, N.J. Dudney, J. Kiggans, K. Hong, A. J. Rondinone, C. Liang, Anomalous high ionic conductivity of nanoporous β-Li₃PS₄, J. Am. Chem. Soc. 135 (2013) 975–978.
- [21] Y. Seino, T. Ota, K. Takada, A. Hayashi, M. Tatsumisago, A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries, Energy Environ. Sci. 7 (2014) 627–631.
- [22] E. Quartarone, P. Mustarelli, Electrolytes for solid-state lithium rechargeable batteries: recent advances and perspectives, Chem. Soc. Rev. 40 (2011) 2525–2540.
- [23] B. Kumar, S.J. Rodrigues, S. Koka, The crystalline to amorphous transition in peobased composite electrolytes: role of lithium salts, Electrochim. Acta 47 (2002) 4125–4131.
- [24] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nanocomposite polymer electrolytes for lithium batteries, Nature 394 (1998) 456–458.
- [25] C. Ma, J. Zhang, M. Xu, Q. Xia, J. Liu, S. Zhao, L. Chen, A. Pan, D.G. Ivey, W. Wei, Cross-linked branching nanohybrid polymer electrolyte with monodispersed TiO₂ nanoparticles for high performance lithium-ion batteries, J. Power Sources 317 (2016) 103–111.
- [26] C.W. Lin, C.L. Hung, M. Venkateswarlu, B.J. Hwang, Influence of TiO₂ nanoparticles on the transport properties of composite polymer electrolyte for lithiumion batteries, J. Power Sources 146 (2005) 397–401.
- [27] L.V.N.R. Ganapatibhotla, J.K. Maranas, Interplay of surface chemistry and ion content in nanoparticle-filled solid polymer electrolytes, Macromolecules 47 (2014) 3625–3634.
- [28] X. Chen, W. He, L.-X. Ding, S. Wang, H. Wang, Enhancing interfacial contact in all solid state batteries with a cathode-supported solid electrolyte membrane framework, Energy Environ. Sci. 12 (2019) 938–944.
- [29] S. Liu, H. Wang, N. Imanishi, T. Zhang, A. Hirano, Y. Takeda, O. Yamamoto, J. Yang, Effect of Co-doping nano-silica filler and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide into polymer electrolyte on Li dendrite formation in Li/poly(ethylene oxide)-Li(CF₃SO₂)₂N/Li, J. Power Sources 196 (2011) 7681–7686.
- [30] J. Hassoun, B. Scrosati, Moving to a solid-state configuration: a valid approach to making Lithium-sulfur batteries viable for practical applications, Adv. Mater. 22 (2010) 5198–5201.
- [31] Y. Zhao, Z. Huang, S. Chen, B. Chen, J. Yang, Q. Zhang, F. Ding, Y. Chen, X. Xu, A promising PEO/LAGP hybrid electrolyte prepared by a simple method for allsolid-state lithium batteries, Solid State Ion. 295 (2016) 65–71.
- [32] C.-Z. Zhao, X.-Q. Zhang, X.-B. Cheng, R. Zhang, R. Xu, P.-Y. Chen, H.-J. Peng, J.-Q. Huang, Q. Zhang, An anion-immobilized composite electrolyte for dendrite-free lithium metal anodes, Proc. Natl. Acad. Sci. 114 (2017) 11069–11074.
- [33] L. Chen, Y. Li, S.-P. Li, L.-Z. Fan, C.-W. Nan, J.B. Goodenough, PEO/garnet composite electrolytes for solid-state lithium batteries: from "ceramic-in-polymer" to "polymer-in-ceramic", Nano Energy 46 (2018) 176–184.
- [34] F. Croce, L. Persi, F. Ronci, B. Scrosati, Nanocomposite polymer electrolytes and their impact on the lithium battery technology, Solid State Ion. 135 (2000) 47–52.
- [35] M. Marcinek, A. Bac, P. Lipka, A. Zalewska, G. Żukowska, R. Borkowska, W. Wieczorek, Effect of filler surface group on ionic interactions in

 $PEG-LiClO_4-Al_2O_3$ composite polyether electrolytes, J. Phys. Chem. B 104 (2000) 11088–11093.

- [36] P.P. Chu, M. Jaipal, Reddy, Sm₂O₃ composite PEO solid polymer electrolyte, J. Power Sources 115 (2003) 288–294.
- [37] W. Liu, D. Lin, J. Sun, G. Zhou, Y. Cui, Improved lithium ionic conductivity in composite polymer electrolytes with oxide-ion conducting nanowires, ACS Nano 10 (2016) 11407–11413.
- [38] P. Lun, P. Liu, H. Lin, Z. Dai, Z. Zhang, D. Chen, Ionic conductivity promotion of polymer membranes with oxygen-ion conducting nanowires for rechargeable lithium batteries, J. Membr. Sci. 580 (2019) 92–100.
- [39] H. Chen, D. Adekoya, L. Hencz, J. Ma, S. Chen, C. Yan, H. Zhao, G. Cui, S. Zhang, Stable seamless interfaces and rapid ionic conductivity of Ca–CeO₂/LiTFSI/PEO composite electrolyte for high-rate and high-voltage all-solid-state battery, Adv. Energy Mater. 10 (2020), 2000049.
- [40] N. Wu, P.-H. Chien, Y. Qian, Y. Li, H. Xu, N.S. Grundish, B. Xu, H. Jin, Y.-Y. Hu, G. Yu, J.B. Goodenough, Enhanced surface interactions enable fast Li⁺ conduction in oxide/polymer composite electrolyte, Angew. Chem. Int. Ed. 59 (2020) 4131–4137.
- [41] K. Fu, Y. Gong, J. Dai, A. Gong, X. Han, Y. Yao, C. Wang, Y. Wang, Y. Chen, C. Yan, Y. Li, E.D. Wachsman, L. Hu, Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries, Proc. Natl. Acad. Sci. 113 (2016) 7094–7099.
- [42] J. Bae, Y. Li, F. Zhao, X. Zhou, Y. Ding, G. Yu, Designing 3D nanostructured garnet frameworks for enhancing ionic conductivity and flexibility in composite polymer electrolytes for lithium batteries, Energy Storage Mater. 15 (2018) 46–52.
- [43] W. Liu, N. Liu, J. Sun, P.-C. Hsu, Y. Li, H.-W. Lee, Y. Cui, Ionic conductivity enhancement of polymer electrolytes with ceramic nanowire fillers, Nano Lett. 15 (2015) 2740–2745.
- [44] J. Bae, Y. Li, J. Zhang, X. Zhou, F. Zhao, Y. Shi, J.B. Goodenough, G. Yu, A 3D nanostructured hydrogel-framework-derived high-performance composite polymer lithium-ion electrolyte, Angew. Chem. Int. Ed. 57 (2018) 2096–2100.
- [45] P. Zhu, C. Yan, M. Dirican, J. Zhu, J. Zang, R.K. Selvan, C.-C. Chung, H. Jia, Y. Li, Y. Kiyak, N. Wu, X. Zhang, Li_{0.33}La_{0.557}TiO₃ ceramic nanofiber-enhanced polyethylene oxide-based composite polymer electrolytes for all-solid-state lithium batteries, J. Mater. Chem. A 6 (2018) 4279–4285.
- [46] X. Wang, Y. Zhang, X. Zhang, T. Liu, Y.-H. Lin, L. Li, Y. Shen, C.-W. Nan, Lithiumsalt-rich PEO/Li_{0.3}La_{0.557}TiO₃ interpenetrating composite electrolyte with threedimensional ceramic nano-backbone for all-solid-state lithium-ion batteries, ACS Appl. Mater. Interfaces 10 (2018) 24791–24798.
- [47] Z. Wan, D. Lei, W. Yang, C. Liu, K. Shi, X. Hao, L. Shen, W. Lv, B. Li, Q.-H. Yang, F. Kang, Y.-B. He, Low resistance–integrated all-solid-state battery achieved by Li₇La₃Zr₂O₁₂ nanowire upgrading polyethylene oxide (PEO) composite electrolyte and peo cathode binder, Adv. Funct. Mater. 29 (2019), 1805301.
- [48] F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, Electron localization determines defect formation on ceria substrates, Science 309 (2005) 752–755.
- [49] L. Zhu, P. Zhu, Q. Fang, M. Jing, X. Shen, L. Yang, A novel solid PEO/LLTOnanowires polymer composite electrolyte for solid-state lithium-ion battery, Electrochim. Acta 292 (2018) 718–726.
- [50] Y.-C. Zhang, Z. Li, L. Zhang, L. Pan, X. Zhang, L. Wang, Fazal-e-Aleem, J.-J. Zou, Role of oxygen vacancies in photocatalytic water oxidation on ceria oxide: experiment and DFT studies, Appl. Catal. B Environ. 224 (2018) 101–108.
- [51] Y. Zhao, Y. Wang, A. Mathur, Y. Wang, V. Maheshwari, H. Su, J. Liu, Fluoridecapped nanoceria as a highly efficient oxidase-mimicking nanozyme: inhibiting product adsorption and increasing oxygen vacancies, Nanoscale 11 (2019) 17841–17850.
- [52] Z. Sun, Y. Li, S. Zhang, L. Shi, H. Wu, H. Bu, S. Ding, g-C₃N₄ nanosheets enhanced solid polymer electrolytes with excellent electrochemical performance, mechanical properties, and thermal stability, J. Mater. Chem. A 7 (2019) 11069–11076.
- [53] W. Li, S. Zhang, B. Wang, S. Gu, D. Xu, J. Wang, C. Chen, Z. Wen, Nanoporous adsorption effect on alteration of the Li⁺ diffusion pathway by a highly ordered porous electrolyte additive for high-rate all-solid-state lithium metal batteries, ACS Appl. Mater. Interfaces 10 (2018) 23874–23882.
- [54] S. Duluard, J. Grondin, J.-L. Bruneel, I. Pianet, A. Grélard, G. Campet, M.-H. Delville, J.-C. Lassègues, Lithium solvation and diffusion in the 1-butyl-3methylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquid, J. Raman Spectrosc. 39 (2008) 627–632.
- [55] J. Huang, A.F. Hollenkamp, Thermal behavior of ionic liquids containing the FSI anion and the Li⁺ cation, J. Phys. Chem. C 114 (2010) 21840–21847.
- [56] N. Chen, Y. Dai, Y. Xing, L. Wang, C. Guo, R. Chen, S. Guo, F. Wu, Biomimetic antnest ionogel electrolyte boosts the performance of dendrite-free lithium batteries, Energy Environ. Sci. 10 (2017) 1660–1667.
- [57] D.G. Mackanic, W. Michaels, M. Lee, D. Feng, J. Lopez, J. Qin, Y. Cui, Z. Bao, Crosslinked poly(tetrahydrofuran) as a loosely coordinating polymer electrolyte, Adv. Energy Mater. 8 (2018), 1800703.
- [58] W. Li, C. Sun, J. Jin, Y. Li, C. Chen, Z. Wen, Realization of the Li⁺ domain diffusion effect via constructing molecular brushes on the LLZTO surface and its application in all-solid-state lithium batteries, J. Mater. Chem. A 7 (2019) 27304–27312.
- [59] S. Suriyakumar, S. Gopi, M. Kathiresan, S. Bose, E.B. Gowd, J.R. Nair, N. Angulakshmi, G. Meligrana, F. Bella, C. Gerbaldi, A.M. Stephan, Metal organic

X. Ao et al.

framework laden poly(ethylene oxide) based composite electrolytes for all-solidstate Li-S and Li-metal polymer batteries, Electrochim. Acta 285 (2018) 355–364.

- [60] V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, Crystal orbital hamilton population (COHP) analysis as projected from plane-wave basis sets, J. Phys. Chem. A 115 (2011) 5461–5466.
- [61] R. Dronskowski, P.E. Blöchl, Crystal orbital hamilton populations (COHP): energyresolved visualization of chemical bonding in solids based on density-functional calculations, J. Phys. Chem. 97 (1993) 8617–8624.



Xin Ao is currently a postdoctoral fellow at Shenzhen University. He received his Ph.D. from Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China. His research interests are synthesis and characterization of all-solid-state electrolytes for high performance Li/Na batteries and energy applications.



Xiaotao Wang is currently a postdoctoral fellow at Shenzhen University. He received his B.Sc., M.Sc., and Ph.D. at Xi'an Jiaotong University, Xi'an, Shaanxi, China. His research interests include the structure and multiferroic ceramics.



Jiewen Tan received the master's degree from South China University of technology, Guangdong GuangZhou, P.R. China in 2020. He is currently a Ph.D. student at Xi'an Jiaotong University, China. His research interests mainly include preparation and characterization of high performance solid polymer electrolyte for lithium batteries.



Shaolong Zhang is currently a postdoctoral fellow at Shenzhen University. He received his Ph.D. degree in China University of Petroleum (Beijing) in 2015. His research interest focuses on design and synthesis of novel nanomaterials, and their applications in heterogeneous catalysis and electrocatalysis.



Chenliang Su is currently a professor at Shenzhen University. He received his BS degree (2005) and Ph.D. degree (2010) from the Department of Chemistry at the Zhejiang University, China. After that he worked as a research fellow at the Advanced 2D Materials and Graphene Research Centre at the National University of Singapore (2010–2015). His current interests include the study of nanostructured materials for heterogeneous catalysis and energy applications.



Lei Dong received his Ph.D. degree from State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University in 2015. He then worked at Fudan University as a postdoctoral fellow. During the year 2016–2017, he visited National University of Singapore to continue his research on graphene preparation and lithium battery in collaboration with professor Kian Ping Loh. He is currently a research assistant professor in ShanghaiTech University. His research interests include graphene, lithium batteries, 2D materials and single atom catalysis.



Mingxue Tang is currently a principal investigator (PI) and Staff Scientist at Center for High Pressure Science and Technology Advanced Research (HPSTAR). Dr. Tang's research interests mainly focus on developing novel NMR/EPR techniques for characterization of materials synthesized under extreme conditions. Additionally, his team is aiming for designing nondestructive tools, in situ NMR/EPR, to understand the mechanism of the materials under operation (electrochemical cycling). Dr. Tang graduated from Zhejiang University and obtained his Ph.D. degree from University of Paderborn. Years' postdoctoral training was followed in CNRS (France) and the National High Magnetic Field Laboratory (US) before he joined HPSTAR.



Zhongchang Wang received his Ph.D. in materials science from the University of Tokyo in Japan (2007). He thereafter spent two years as a research associate at Tohoku University (Japan) and subsequently three years as an assistant professor. In 2013, he was promoted to associate professor at Tohoku University. Since 2017, He started as a principal investigator (PI) and senior staff researcher at INL, and established a research group of "Atomic Manipulation for Quantum Nanotechnology" at INL. He is going to work on structure-property interplay of two-dimensional materials and nanomaterials at the atomic scale.



Bingbing Tian received his Bachelor Degree from Zhengzhou University (China) in 2008, Master degree from South China University of Technology (China) in 2011 under the supervision of Prof. Haihui Wang, and Doctor degree from Université Pierre et Marie Curie (France) in 2014 under the supervision of Prof. Philippe Marcus. Then he was a Postdoctoral Research Fellow in National University of Singapore from 2015 to 2017. He is currently an Assistant Professor at the Institute of Microscale Optoelectronics in Shenzhen University. His research activities are focused on energy storage devices including lithium ion batteries, lithium sulfur batteries and allsolid-state batteries.

Nano Energy 79 (2021) 105475



Haihui Wang received his Ph.D. from Dalian Institute of Chemical Physics (the Chinese Academy of Sciences) in 2003. After a one and half years study as an Alexander von Humboldt Research Fellow in the Institute of Physical Chemistry and Electrochemistry, Leibniz University of Hannover, Germany, he continued his studies there as a postdoctoral fellow in 2005. Now he is a full professor at the South China University of Technology, China. His interests focus on inorganic membranes, membrane reactor, and energy materials.