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Supporting Information

Defect-rich Carbon Induced Built-in Interfacial Electric Field Accelerating Ion-conduction towards Superior-stable Solid-state Batteries†

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Methods

Materials

P(VDF-HFP) (Mw= 800,000) was dried at 90 °C overnight before utilization. NaTFSI and Pyr₁₃TFSI were obtained from Chilwee and stored in a glove box. Polyvinyl alcohol (PVA), TEOS, formic acid, Na₃V₂(PO₄)₃ (NVP), NaFePO₄ (NFP), Na₄Fe₃(PO₄)₂P₂O₇ (NFPP), NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ (NFM), 3,4,9,10- perylene tetracarboxylic diimide, LiFePO4 (LFP), LiNi_{0.9}Co_{0.05}Mn_{0.05}O₂ (NMC9055), super P, N-methyl-2-pyrrolidone (NMP, analytical grade), ethanol, and acetone (purity > 99 %) were obtained from Aladin.

Synthesis of D-CSE-pre fiber

First, precursor nanofiber membrane was fabricated. TEOS, deionized water, and formic acid were mixed with a molar ratio of 1: 8.1: 0.3 and stirred for 10 h at room temperature to form a silica sol. PVA was dissolved in deionized water and stirred at 80 °C to form a 10 wt.% polymer template solution. The electrospinning solution was prepared by mixing the polymer template solution and silica sol with a mass radio of 1:3. The scalable electrospinning was proceeded at a voltage of 30 kV with a collector distance of 20 cm. Then, the electrospun precursor nanofibrous membrane was calcined at 500 °C for 2 h with a heating rate of 5 °C min⁻¹ at air atmosphere to obtain a flexible SiO₂@DC membrane named D-CSE-pre. For comparison, SiO₂ membrane without C was prepared on the same procedure as above except that stabilizing the membrane at 600 °C for 2 h named PVS-pre.

Preparation of D-CSE composite solid electrolyte sodium based

PVDF-HFP powder was dried under vacuum at 100 °C overnight to remove moisture. PVDF-HFP with a mass radio of 5 wt.% was dissolved in an NMP and acetone mixture (5:5 w/w) to form a homogeneous solution. Then, NaTFSI and Pyr₁₃TFSI were added and stirred for 1 h (PVDF-HFP: NaTFSI: Pyr₁₃TFSI = 2.5: 1 :4 w/w/w). Next, the completely homogeneous solution was poured on glass and cast it with a blade (50 μ m) at a uniform speed. Besides, the pure PVDF-HFP solution containing NaTFSI and Pyr₁₃TFSI was also prepared, and all the prepared electrolytes were dried in an air-circulating at 80 °C for 12 h and in a vacuum oven at 80 °C for 12 h. Finally, the D-CSE, PVS and PVDF-HFP composite electrolyte membrane was peeled off from the Teflon plate for tests.

Characterization of materials

Powder X-ray diffractometer (XRD, HY DX-2700BH) with a Cu K radiation (2 θ cope from 10 to 70°, 5° min⁻¹) was used to determine the crystal structure of the samples.

Thermogravimetric analysis (TGA) under air atmosphere were collected on a STA7200RV instrument from 30 °C to 800 °C with a heating rate of 5 °C min⁻¹. Differential scanning calorimetry (DSC) measurements were conducted by a DSC TA Q200 with a heating rate of 5 °C min⁻¹. The morphologies were investigated by SEM (scanning electron microscopy) ZEISS Gemini 300 with 5 kV electron energy. Qualitative or quantitative analysis of elements contained in tiny regions was carried out by assembling an X-ray energy dispersion spectrometer (EDS). Fourier transform infrared spectroscopy (FT-IR) spectra were performed in a Thermo Nicolet AVATAR 360 from 2000 to 400 cm⁻¹. The solid-state ²³Na nuclear magnetic resonance (ssNMR) were performed with a Bruker Avance Neo 400WB spectrometer. Chemical environments of the polymer electrolyte were checked by the Raman spectrometer with an exciting laser of 532 nm. (HR800 Raman spectrometer, Horiba Jobin-Yvon Ltd). The split-peak fitting was operated in Origin 2020 pro via the functional of Multiple Peak Fit while all the values of R-square are larger than 0.99.

Cryogenic-(scanning) transmission electron microscopy (cryo-TEM) characterizations were carried out using a JEOL JEM-F200 microscope under cryogenic temperatures ($-180 \,^{\circ}$ C) at 200 kV. The samples for cryo-TEM characterizations were prepared by directly depositing Na metal on a TEM grid at a current density of 0.5 mA cm⁻² for 0.5 h. The grid was rinsed by EC slightly twice and dried in the vacuum mini chamber of the glove box. Then it was loaded on the cryo-TEM holder (Fischione 2550) equipped with a tip retraction device in the glove box and transferred into the JEOL JEM-F200 microscope without any air exposure with the help of a sealing sleeve.

Electrochemical measurements

Ionic conductivity was determined by EIS after placing the solid electrolyte between two electrodes (stainless steel) contacts in a CR2025 coin cell without liquid electrolyte. The tests were performed in the range from 0 to 100 °C with a step size of 5 °C min⁻¹ via alternating-current (AC) impedance from 0.1 Hz to 10 kHz, and σ was calculated by electrochemical impedance spectra (EIS) using the equation:

$$\sigma = \frac{L}{S \cdot R_b} \tag{1}$$

Where R_b is the bulk resistance; L is the thickness; S is surface area of SPEs. The electrical conductivity of the solid electrolyte is calculated using the equation:

$$\gamma = \frac{I_s L}{US} \tag{2}$$

Activation energy E_a can be calculated according to the Arrhenius equation:

$$\sigma = AT^{-1}e^{\frac{-Ea}{RT}}$$
(3)

The value of A is related to the effective charge carrier concentration.

The electrochemical stability window was tested by linear sweep voltammetry (LSV) on a Na||CSEs||stainless steel cell from 0 to 6.5 V by CHI604A at a scan rate of 0.2 mV s⁻¹.

The transference number (t) was tested in symmetric sodium cell using CHI604A at room temperature by a combination of DC polarization and AC impedance measurement. A DC potential ($\Delta V=10 \text{ mV}$) was applied for 2000 s to gain the initial and steady currents. Meanwhile, the AC impedance spectra of the same cell were measured before and after polarization. The value of lithium/sodium transference number (${}^{t}_{Li/Na^{+}}$) has been calculated by the equation:

$$t_{Li/Na^{+}} = \frac{I_{s}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{s}R_{s})}$$
(4)

Where R_0 and R_s are the AC impedances before and after polarization, respectively. I_0 and I_s are the initial and steady currents respectively.

To further explore the compatibility of solid electrolytes with Na, the sodium striping/plating experiments employing the same cell was conducted in a LAND CT2001A battery test system at ambient temperature with the current density of 0.05 to 1.0 mA cm⁻² (the sum of the charge and discharge times was 2 h).

The cathode electrode was prepared by mixed NVP (80 wt %), Super-P (10 wt %) and PVDF (10 wt %, as binder) in 1-Methyl-2-pyrrolidinone solvent to form a homogeneous slurry. The slurry was cast onto a carbon-coated Aluminum foil, then dried in a vacuum oven at 80 °C overnight. The mass loading of NVP is around 2.0 mg cm⁻² and the thickness is around 75 μ m. CR2025-type coin cell was assembled by using the NVP electrode as cathode, CSEs as separator, and Na metal (50 µm) as anode with the addition of 2 µL liquid electrolyte (NC-008:1 M NaClO4 in DEC: EC = 1:1 Vol% with 5% FEC). The calendering pressure is 10.6 Mpa. In Na||D-CSE||NVP pouch cell, we use "NC-008" (1 M NaClO₄ in DEC: EC = 1:1 Vol% with 5% FEC) mixed with $Pyr_{13}TFSI$ as the liquid electrolyte (NC-008: $Pyr_{13}TFSI = 1:2$). We add the liquid electrolyte according to a special ratio $(4 \,\mu L \,mg^{-1})$ in the Na||D-CSE||NVP pouch cell. The electrochemical performance of assembled cells was examined with a Land CT2001A testing system (Wuhan Jinnuo Electronics, Ltd.). Unless otherwise noted, all the cells were tested at RT (~25 °C). For Na/NVP batteries, the cyclic voltammetry (CV) test was investigated by a CHI604A under 0.1 mV s⁻¹ scan rate with a voltage range of 2.0 to 3.8 V at RT. The galvanostatic charge-discharge (GCD) profiles and charge/discharge cycles of assembled batteries were investigated by a LAND CT2001A battery test system, where 1 C equal to 117

mA g⁻¹. All cells were assembled or disassembled in an argon-filled glovebox. The other SMBs and LMBs are assembled with the same workflows.

Modeling simulation

This calculation adopted the finite element method and utilized the COMSOL Multiphysics AC-DC module steady-state analysis method to simulate the evanescent electric field inside the materials of three models under steady-state power supply. Firstly, three geometric models of fiber structures were established, and the relative dielectric constants of the materials in the models were set at potential. We used terminal 1 as the emission source (input+1V) and port 2 as the output (-1V) to obtain the simulated electric field line distribution, then calculated the potential induction and electric field line distribution of the electric field in the material based on the steady state equation.

Molecular Dynamics Simulation

The partial charge of NaTFSI $\,$ PVDF-HFP and Pyr₁₃TFSI molecule was calculated using Gaussian 16 code and the 6-311g(d,p) basis functions were applied¹. The OPLS-AA force field² and Auxiliary Tools of Force Field (AuToFF) were used to parametrize all atoms, such as the bond parameters, angle parameters and the dihedral angles, and so on. The atomic charges of SiO₂ were estimated by the Density Derived Electrostatic and Chemical (DDEC) method³ based on density functional theory calculations using the Vienna *Ab Initio* Simulation Package (VASP)⁴. The force field parameters of silicon atoms are taken from the UFF force field⁵.

The solvation structures of sodium ions on pure electrolyte (system 1), pure SiO_2 (system 2) and 10% C-coated SiO_2 (system 3) were simulated by molecular dynamics (MD) simulation. The 10% C-coated SiO_2 is constructed by loading less graphene on the SiO_2 surface.

The monomer ratio of PVDF-HFP \cdot NaTFSI \cdot Pyr₁₃TFSI=5 : 2 : 8. In system 1, 100 PVDF-HFP \cdot 40 NaTFSI and 160 Pyr₁₃TFSI molecules were randomly inserted into a cube box with a side length of 7.0 nm. In system 1 and system 2, the same number of electrolyte molecules are added on both sides of pure SiO₂ and 10% defect-rich carbon-coated SiO₂ respectively, and the total number of electrolyte molecules is the same as that of system 1.

The MD simulations were performed in the GROMACS 2021 software package^{6, 7}. The steepest descent method was applied to minimize the initial energy for each system with a force tolerance of 1 kJ/(mol⁻¹ nm⁻¹) and a maximum step size of 0.002 ps before MD calculations⁸. In all the three directions, periodic boundary conditions were imposed. Leapfrog algorithm was used to integrate the Newtonian equation of motion. Then, it was heated to 298.15 k under canonical (NVT) ensemble via Nose-Hoover thermostat barostat for 20 ps MD simulation.

Finally, 20 ns MD simulation was performed to collect the trajectory coordinates of molecules under NPT ensemble. Diffusion coefficient of Na⁺ were calculated based on the mean–squared displacement (MSD)

In NPT simulations, the pressure was maintained at 1 bar by the Berendsen barostat in an isotropic manner⁹ and the temperature was maintained by the V-rescale thermostat at 298.15 K. The Particle-Mesh-Ewald (PME) with a fourth-order interpolation was used to evaluate the electrostatic interactions and whereas a cutoff of 1.0 nm was employed to calculate the short-range van der Waals interactions¹⁰.

Density functional theory

We have employed the first-principles tool—Vienna Ab initio Simulation Package(VASP) ^{11, 12}to perform all density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)¹³ formulation. We have chosen the projected augmented wave (PAW) potentials¹⁴ to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. For the optimization of both geometry and lattice size, the Brillouin zone integration was performed with a $1 \times 1 \times 1$ Gamma centered sampling¹⁵. The self-consistent calculations applied a convergence energy threshold of 10⁻⁵ eV. The equilibrium geometries and lattice constants were optimized with maximum stress on each atom within 0.02 eV Å⁻¹. The 17 Å vacuum layer was normally added to the surface to eliminate the artificial interactions between periodic images. The weak interaction was described by DFT+D3 method using empirical correction in Grimme's scheme¹⁶.



Figure 1| TGA curves of PVA/TEOS.

As seen in the TGA curves, PVA/TEOS has no weight loss after 600 °C, which means carbon components have volatilized completely. To reserve a given mass of defect-rich carbon on SiO₂ nanofibers, we choose 500 °C as the test temperature.

In this article, the defect-rich carbon comes from the low-temperature carbonization process of organic PVA. So far, integrating heteroatoms on carbon is a main way in the synthesis of carbon defects. Pyrolysis and post-modification synthesis are the most widely used strategies in complex carbon defect synthesis. For the first method, the component of precursor is critical, which generally contains heteroatoms that is easy to be incorporated into carbon lattice in the pyrolysis process. Meanwhile, the complicated reconstruction process in the pyrolysis process is favor of the formation of carbon defect sites^{17, 18}. Therefore, we choose the low-temperature carbonization of PVA to produce the defect-rich carbon. The calcination temperature of 500 °C is not high enough to eliminate all oxygen atoms and the rest oxygen atom plays a role in heteroatom doping. Besides, the oxidation process of air calcination causes more defects to form¹⁹. In this way, the defect-rich carbon is successfully designed and constructed.



Figure 2| SEM images and EDS elemental mappings of C, Si and O in (a) D-CSE-pre and (b) PVS-pre.



Figure 3| TEM image and EDS elements mapping of D-CSE-pre. In Figure S3, We have tried to distinguish the boundary line between carbon and SiO₂ in this TEM image of the D-CSE-precursor by EDS elements mapping. However, we use the ultrathin copper grid as the sample carrier, which contains carbon and influences the result of elements mapping. Moreover, EDS test is inaccurate for light elements with lower energy such as C, O, etc. The boundary line between carbon and SiO₂ in Figure S3c could be observed more clearly.



Figure 4| TEM images of PVS-pre.



Figure 5| XRD patterns of D-CSE-pre and PVS-pre. In Fig. S5, the peak between 20-30 degree referring to carbon material in D-CSE-pre has

higher intensity than PVS-pre, which proves the existence of the defect-rich carbon in D-CSE-

pre.



Figure 6 Raman spectra of D-CSE-pre and PVS-pre. In Fig. S6, the Characteristic peak of carbon material in D-CSE-pre is obvious, which

certifies the existence of the defect-rich carbon in D-CSE-pre.



Figure 7| SEM image of D-CSE. (inset: optical photo of D-CSE).



Figure 8| (a) Tensile stress-strain curves and (b) Young's modulus value of D-CSE and PVS.



Figure 9| Photographs of the D-CSE that was folded and scrunched.



Figure 10| Flammability test (top: D-CSE, bottom: PVDF-HFP)



Figure 11 | The top and side views of the defect-rich C, PVDF-HFP, defect-rich C-PVDF-HFP.



Figure 12 | The DOS of bulk defect-rich C, PVDF-HFP and the defect-rich C/PVDF-HFP.



Figure 13 | Raman patterns of PVS.



Figure 14| XRD patterns of D-CSE, PVS and PVDF-HFP powder.



Figure 15| FTIR spectra of D-CSE, PVS and PVDF-HFP powder.



Figure 16 DSC profiles of D-CSE, PVS and PVDF-HFP.



Figure 17| TGA curves of D-CSE, PVS and PVDF-HFP.



Figure 18 Nyquist plots of (a) SS||PVDF-HFP||SS, (b)SS||D-CSE||SS, (c)SS||PVS||SS at various temperatures, (d) Ionic conductivity of D-CSE, PVS and PVDF-HFP.



Figure 19 Electronic conductivity of CSEs at room temperature.

We have tested the electronic conductivity of CSEs to further make sure there is no electron leakage in CSE-DC. Via the electrochemical impedance spectroscopy (EIS) tests with only stainless-steel current collectors, it could be noticed that the starting points of the lines which represents the bulk electrolyte resistance is decreasing with the introduction with the defect-rich carbon (Figure S18a). Besides, there is no semi-circle appearing in CSE-DC, which is corresponding to the leakage of electrons through percolated domains (Figure S18b). The CSE-DC has the highest electronic conductivity due to the addition of carbon, but still in the reasonable range.



Figure 20 (a-c) The chronoamperometry profiles of symmetric Na||CSEs||Na cell with potential steps of 100 mV at RT (inset: The EIS spectra the range from 10^5 to 0.1 Hz). (d) Na⁺ transference number of CSEs.

The increase of the transference number could be attributed to some points as follows:

1) Thorough dissociation of sodium salts. The introduction of defect-rich carbon improves the permittivity of D-CSE, which could significantly accelerate the dissociation of sodium salts and influence the coordination state of Na⁺ in CSEs^{20202020202020202020191817171718[18][18]}. Besides, the formed built-in interfacial electric field between the defect-rich carbon and PVDF-HFP could provide extra driving force to free more cations

2) Strong cation transportation. In D-CSE, Na⁺ could transport in two ways. First, the builtin IEF could build effective ion-transport channels, and provide an extra driving force for iontransportation. Second, the combination of PVDF-HFP with NaTFSI acts as the inert framework, and the ionic liquid $Pyr_{13}TFSI$ softens the polymer chains by weakening the molecule force. The synergistic effect of three components provides additional pathways for ion transport.

3) Restriction on TFSI⁻ anions. After introducing SiO₂ nanofibers, the Na⁺ transference number can be significantly enhanced because SiO₂ can block TFSI⁻ anions and restrict their migration due to Lewis acids and bases^{21, 22}.

In general, the transference number is remarkably improved with the addition of defectrich carbon.



Figure 21 | LSV profiles of CSEs at 0.2 mV s⁻¹ at RT



Figure 22| 3D snapshots of PVS.



Figure 23| The radial distribution function g(r) analyses and the coordination number in (a) PVDF-HFP, (b) D-CSE and (c) PVS derived from MD simulation.



Figure 24| Simulation of l potential distribution and current density distribution conducted by COMSOL Multiphysics of aggregated carbon particles and individual SiO₂ networks.



Figure 25 | AFM images of (a) D-CSE; (b) PVDF-HFP+DC.



Figure 26| (a) Nyquist plots of SS||PVDF-HFP+DC||SS, (b) Arrhenius plots of SS||PVDF-HFP+DC||SS. (c) The chronoamperometry profiles of symmetric Na|| PVDF-HFP+DC ||Na cell with potential steps of 100 mV at RT.



Figure 27| Voltage profiles of Na||D-CSE||Na batteries from 0.05 to 1 mA cm⁻².



Figure 28| Voltage profiles CSEs based symmetric cells at 0.05 mA cm⁻² at RT and zoomedin plots within different cycles.



Figure 29 Zoomed-in voltage profiles CSEs based symmetric cells at 1 mA cm⁻² at RT within (a) 100-110 h, (b) 500-510 h, (c) 900-910 h.



Figure 30| Nyquist curves of (a) Na||PVS||Na and (b) Na||PVDF-HFP||Na at selected cycles.



Figure 31 Coulombic efficiency curves based on different Na CSEs Cu batteries.



Figure 32| In situ observations of the symmetric (a_1) Na||PVDF-HFP||Na, (b_1) Na||D-CSE||Na and (c_1) Na||PVS||Na cell at the current density of 10 mA cm⁻². SEM images of the cycled SSMBs from (a_2) Na||PVDF-HFP||Na, (b_2) Na||D-CSE||Na and (c_2) Na||PVS||Na cell.



Figure 33| Cryo-TEM image of the plated Na and SEI layer formed in Na||PVDF-HFP||Na and Na||PVS||Na batteries .



Figure 34 XPS depth profiling analysis of the SEI layer in Na||D-CSE||Na cell.



Figure 35 | C 1s XPS spectra of the SEI layer from the sodium anode surface to a sputtering time of 45 s of the three SPEs.



Figure 36| O 1s XPS spectra of the SEI layer from the sodium anode surface to a sputtering time of 45 s of the three SPEs.



Figure 37| F 1s XPS spectra of the SEI layer from the sodium anode surface to a sputtering time of 45 s of the three SPEs.

NaF is regarded as the key component in the SEI of sodium metal, which plays an important role in governing the transport and homogeneous deposition of Na⁺ ions^{23, 24}. The NaF in the SEI layer could make uniform deposition and dissolution of Na metal and also improve the long-standing cycling stability of batteries at room temperature^{25, 26}. Owing to its high Young's modulus, high surface energy, and abundant Na-ion flux, the SEI effectively dissipates the local current density to tune the Na nucleation in a uniform and low-volume manner, reducing the tendency of the moss-like dendrite growth²⁷. However, NaF has high Na⁺ diffusion energy barriers and low ionic conductivity. While Na₂O has a lower surface diffusion energy barrier to Na⁺, thereby lowering the nucleation overpotential, accelerating the interfacial Na⁺ transfer kinetics, and exhibiting excellent electrochemical performance²⁸. In our work, the main compositions of the SEI layer (NaF and Na₂O) in the D-CSE based symmetric cell prevent electrolyte consumption and Na dissolution, providing a compact interface with high Na⁺ conductivity, and inhibiting Na dendrite in coordination.



Figure 38 CV curves of (a) Na||PVDF-HDP||NVP and (b) Na||PVS||NVP batteries at a scan rate of 0.1 mV s⁻¹.



Figure 39| Typical GITT profiles for the charge/discharge process of (a)Na||PVDF-HFP||NVP, (b) Na||D-CSE||NVP and (c) Na||PVS||NVP.



Figure 40| Typical charge-discharge profiles of the SSMBs using (a) D-CSE, (b) PVS and (c) PVDF-HFP at RT at 1.0 C.



Figure 41| Cycling performance of Na||D-CSE||NVP batteries at rates of 5 C and 10 C at RT.



Figure 42 | Typical charge–discharge profiles of the SSMBs using D-CSE at (a) 5 C, (b) 10 C at RT at various cycles.



Na||PVS||NVP batteries at a rate of 0.2 C at RT and typical charge-discharge profiles.



Figure 44| The dQ/dV curves of the (a) Na||PVDF-HFP||NVP and (b) Na||PVS||NVP during the initial 100 cycles.



Figure 45| Rate performance of Na||D-CSE||NVP at 80 °C



Figure 46| Cycling performance of Na||D-CSE batteries with different cathodes at RT.



Figure 47| Cycling performance of Na||D-CSE||NVP batteries with a high active material loading of 8.46 mg cm⁻².





Figure 49| (a) Cycling performance of Na||D-CSE||NVP pouch cell. (b) voltage profiles of Na||D-CSE||NVP pouch cell at RT.



Figure 50| F 1s XPS spectra of the CEI layer from the NVP cathode surface to a sputtering time of 45 s of the three SPEs.



Figure 51 N 1s XPS spectra of the CEI layer from the NVP cathode surface to a sputtering

time of 45 s of the three SPEs.



Figure 52 V 2p+O 1s XPS spectra of the CEI layer from the NVP cathode surface to a sputtering time of 45 s of the three SPEs.



Figure 53 | P 2p XPS spectra of the CEI layer from the NVP cathode surface to a sputtering

time of 45 s of the three SPEs.



Figure 54| Peak contents derived from the XPS spectra of the CEI layer in different CSEs.

Preparation of D-CSE composite solid electrolyte lithium based

PVDF-HFP with a mass radio of 5 wt.% was dissolved in an NMP and acetone mixture (5:5 w/w) to form a homogeneous solution. Then, LiTFSI and Pyr₁₃TFSI were added and stirred for 1 h (PVDF-HFP: LiTFSI: Pyr₁₃TFSI = 2.5: 1 :4 w/w/w). Next, the solution was cast onto the tiled D-CSE-pre on a Teflon plate. The prepared electrolytes were dried in an air-circulating at 80 °C for 12 h and in a vacuum oven at 80 °C for 12 h. Finally, the D-CSE composite electrolyte membrane was peeled off from the Teflon plate for tests.



Figure 55| Nyquist plots of (a) SS||PVDF-HFP||SS, (b)SS||D-CSE||SS, (c)SS||PVS||SS at various temperatures in lithium system, (d) Arrhenius plots.



Figure 56 The chronoamperometry profiles of symmetric Li||CSEs||Li cell with potential steps of 100 mV at RT (inset: The EIS spectra the range from 10⁵ to 0.1 Hz).



Figure 57 |LSV profiles of CSEs at 0.2 mV s⁻¹ at RT in lithium system.



Figure 58| (a) Rate performances of Li||D-CSE||LFP battery. (b) Typical charge–discharge profiles of the Li||D-CSE||LFP battery at RT at various current densities. Cycling performance of Li||D-CSE||LFP batteries at (c) 0.2 C, (d) 2.0 C, (e) 5.0 C. (f) Rate performances of Li||D-CSE||NCM9055 battery. (g) Typical charge–discharge profiles of the Li||D-CSE||NCM9055 battery at RT at various current densities. (h) Cycling performance of Li||D-CSE||NCM9055 battery at 0.5 C.

Supplementary Tables

At%	С	Si	0
PVA/TEOS	41.95	18.08	39.97
D-CSE-pre	18.23	28.52	53.25
PVS-pre	10.45	30.63	58.92

Table 1. Content of C, Si, O of PVA/TEOS, D-CSE-pre and PVS-pre

			Na/Na symmetric battery		Full battery	
CSEs	Thickness (µm)	t _{Na+}	Current (mA cm ⁻²)	Cycling life(h)	Highest Rate &Capacity (mAh g ⁻¹)	Cycle number &Capacity retention
CQSSE ²⁹	127	0.54	0.2	700	1000 mA g ⁻ 1(91)	400-94.1% (1.7 C)
FNCPE ³⁰	76	0.79	0.075	300	3 C (87.6)	200-99.2% (0.5 C)
ATFCGE ³¹	>100	0.61	0.1	1000	3 C (93.2)	87.8% (2 C)
SPF ³²	8	\	0.5	270	\	500-99.3% (1 C)
UT-35SBACE ³³	21	0.91	0.5	200	5 C (82)	100-95.5% (1 C)
EO10-PFPE ³⁴	~100	0.46	0.5	400	2 C (87.7)	940-97.5% (2 C)
ETPTA– NaClO4–QSSE ³⁵	56	0.62	0.1	1000	15 C (55)	1000-96% (1 C) 1000-
ATFPE ³⁶	32	0.63	0.1	650	2 C (68.9)	78.2%
NASCION/PEO ³ 7	95	0.67	0.1	2600	1 C (90.5)	150-89.4% (0.2 C) 1000-
D-CSE (This work)	8.1	0.77	1.0 0.05	1000 3000	20 C (92.1)	86.8% (1 C) 400-96.3% (5 C) 400-97.0% (10.0 C)

 Table 2. Recent progress on CSEs and the corresponding electrochemical performances of

 Na||Na symmetrical cells and full cells

005	ala ancient a companya d	Residual amount (mg kg ⁻	
CSES	cnemical compound	1)	
		,	
PVDF-HFP		N.D.	
PVS	NMP	N.D.	
D-CSE		N.D.	

Table 3. Residual amount of NMP of the three CSEs

Note: N. D. means that the amount of the analyte is below the detection limit of the

instrument, and the detection limit is 5mg L^{-1} .

Materials Species	Purity	Price (\$	Cost (\$ g ⁻¹)	Cost (\$ Wh ⁻¹)		
		g-1)				
This work						
PVDF-HFP	Polymer	Mn~150000	0.03			
NaTFSI	salt	99%	1.27		0.03	
Pyr ₁₃ TFSI	ionic liquid	99%	1.78	0.11		
SiO ₂ @C	filler	/	0.10			
Supplementary ref 10 ³⁸						
PVDF-HFP	polymer	Mn~130000	1.74		/	
NaTFSI	salt	98%	1.99	1.50		
EmimFSI	ionic liquid	98%	1.23			
Nerolin	additive	98%	0.05			
		Supplementary ref 1	1 ³⁹			
PVDF-HFP	polymer	Mn~110000	1.43			
C ₃ mpyrFSI	ionic liquid	98%	2.39	4.08	/	
NaFSI	salt	98%	13.74			
Supplementary ref 12 ⁴⁰						
PEO	polymer	Mv~4000000	0.20			
NaFSI	salt	98%	13.74	19.82	/	
Pyr ₁₄ FSI	ionic liquid	98%	27.48			
	Co	nventional organic liquid	electrolyte			
	1M NaClO ₄ +EC/PC (1:1Vol%) +5%FEC		0.88	/	
	1M NaPF ₆ DME			0.93	/	
Na:4.5V high-voltage organic electrolyte			0.96	/		
1M N	aClO₄+ EC/DMC/EM	IC (1:1:1Vol%) +2%FEC		1.43	/	

Table 4. The cost of D-CSE, other CSEs and conventional organic liquid electrolyte

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