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Carbon dots crosslinked gel polymer electrolytes for dendrite-free and long-cycle lithium metal batteries

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Abstract

Lithium metal batteries (LMBs) with extremely high energy densities have several advantages among energy storage equipment. However, the uncontrolled growth of dendrites and the flammable liquid electrolytes (LEs) often cause safety accidents. All solid-state batteries seem to be the ultimate choice, but solvent-free electrolytes usually fail in terms of conductivity at room temperature. Therefore, gel polymer electrolytes (GPEs) with a simple manufacturing process and high ionic conductivity are considered as the most competitive candidates to resolve the present difficulties. Herein, we design a polymeric network structure via esterification and amidation reactions between polyethylene glycol (PEG) and carbon dots (CDs). After incorporation with polyvinylidene fluoride and some LEs, the as-prepared PEG-CDs composite electrolytes (PCCEs) show a high ionic conductivity of 5.5 mS/cm and an ion transference number of 0.71 at room temperature, as well as good flexibility and thermostability. When the PCCEs are assembled with lithium metal anodes and LiFePO₄ or LiCoO₂ cathodes, both the cycling stability and the retention rate of these LMBs show excellent performance at room temperature.

KEYWORDS

carbon dot, crosslinking structure, gel polymer electrolyte, lithium metal battery, solid electrolyte interface

1 INTRODUCTION

Batteries store electricity in the form of chemical energy, which facilitates the utilization of renewable energy from the sun, wind, and river so as to achieve the goal of carbon neutrality.¹ Among various batteries, lithium metal batteries (LMBs) are expected to be the most efficient and reliable energy storage equipment because _____

of their high energy densities.² Unfortunately, owing to the thermal runway generated by lithium dendrites and flammable liquid electrolytes (LEs), fire and explosion hazards have restricted their practical application since the 1980s. Also, the subsequent improvement strategies, including the use of expensive electrolyte additives and the complex design of lithium interface protection layers, also reduced the availability of LMBs.

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Recently, solid-state and quasi-solid-state electrolytes have shown better performance³ in terms of the safety, processability, and price of LMBs. These new electrolytes include inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and so on. Among them, ISEs have relatively high ion conductivity, but their brittleness limits the processing flexibility and result in poor interfaces with the electrodes. SPEs have much better processability and lower interface impedance, but fail in ionic conductivity at room temperature because their crystalline phases block the ion migration. GPEs are actually the hybrids of SPEs and LEs, which show higher conductivity than SPEs and better safety than LEs,⁴ and thus GPEs have wide applications in practice. To improve GPEs, various additives were used to produce composite electrolytes, such as boron nitride nanosheets,⁵ polyhedral oligomeric silsesquioxane,⁶ and boron nitride nanoflakes.⁷ These inorganic solid additives are able to enhance the mechanical properties, but in the meantime, yield inhomogeneous phases in the composite electrolytes. To overcome this limitation, most of the solid additives are processed into nanoparticles that are as small as possible.⁸ However, nanoparticles have highly reactive surfaces, resulting in unexpected side reactions, and nanoparticles are likely to agglomerate during cycling, which causes instability and decreased battery capacities during long cycles. In terms of the limitation of nanosized additives, it is promising to crosslink nanoparticles with polymers by chemical bonds,^{9,10} which will lead to a polymer-nanoparticle network with many advantages. First, polymers will hinder nanoparticle agglomeration during cycles. Second, polymers will passivate the active groups on the nanoparticles' surface through chemical bonds so as to reduce side reactions. Third, the strong interactions between polymers and nanoparticles will suppress the crystallization of polymers, maintaining the amorphous phases for ion migration. Fourth, ion channels will form along polymer chains and nanoparticle surfaces. Finally, the mechanical properties of GPEs are enhanced to inhibit the growth of lithium dendrites.

Carbon dots (CDs), as a new type of carbon material with special structures and multiple functions, have shown good performance in batteries, supercapacitors, and other electrochemical energy storage equipment. Generally, CDs are mostly used as electrode materials, while their application in electrolytes is scarcely reported. For a long time, CDs were regarded as electronic conductors that cannot be used in electrolytes to avoid short circuit. This concern is reasonable when CDs are derived from conductive graphite or graphene through a top-down preparation. However, most CDs

fabricated from small molecules using the bottom-up strategy have amorphous structures with insulating organic groups outside. When such CDs are added to electrodes, the composite materials must be calcined at high temperatures for CD graphitization. Only after calcination do these CDs become electronically conductive. Some pioneer studies have confirmed the positive effects of CDs in SPEs.¹¹ Herein, we synthesized a new network by crosslinking polyethylene glycol (PEG) and CDs. After incorporation with polyvinylidene fluoride (PVDF) and some LEs, the as-prepared PEG-CD composite electrolytes (PCCEs) show a high ionic conductivity of 5.5 mS/cm and an ion transference number of 0.71 at room temperature, as well as good flexibility and thermostability. Such PCCEs are used in Li/LiFePO₄ (LFP) and Li/LiCoO₂ batteries, which show high retention rates of 96.02% after 300 cycles at 0.5 C and 91.02% after 900 cycles at 2 C, respectively.

2 | EXPERIMENTAL SECTION

2.1 | Synthesis of CDs

CDs were obtained by a classical solvothermal reaction. 2.89 g of citric acid and 1 ml of ethane diamine were dissolved in 10 ml of N,N-dimethylformamide (DMF) in a Teflon-lined stainless-steel (SS) autoclave. Then, the autoclave was transferred into an oven and heated at 170°C for 5 h. Afterwards, the autoclave was cooled to room temperature, and the obtained solution was added to a beaker with 100 ml of ethanol. The solution transformed into a brown suspension, which was centrifuged at a speed of 4000 r/min for 5 min. After pouring out the supernatant liquor, the precipitate was purified by washing with ethanol three times. The obtained product was dried in an oven at 80°C, and then ground into a brown powder.

2.2 | Synthesis of PEG-CDs

PEG with active carboxylic terminal groups (PEG–COOH) was prepared by a carboxylation reaction. PEG, succinic anhydride, and 4-dimethylaminopyridine (DMAP) were dissolved at a molar ratio of 1:2:2 in 50 ml of CH_2Cl_2 , which was stirred in a sealed beaker at room temperature for 3 days. After volatilizing CH_2Cl_2 in a fume cupboard, PEG–COOH was obtained by precipitation with anhydrous ether. 1.5 g of the as-prepared PEG–COOH and 0.3 g of the above CDs were dissolved in 15 ml of DMF, and then 1,3-dicyclohexylcarbodiimide (DCC) and DMAP were added to accelerate the reaction by stirring and refluxing at 80°C in a sealed three-necked flask

(see Supporting Information: Figure S3). This reaction was maintained in a nitrogen atmosphere for 3 days. After the reaction, the solution was poured into a beaker with 60 ml of deionized water, so a white precipitate of dicyclohexylurea was obtained. After removing the precipitate by vacuum filtration, the obtained solution was concentrated by rotary evaporation, followed by dialysis for 10 days using a dialysis bag with a molecular weight of 15,000. The purified aqueous solution was freeze-dried finally to obtain a PEG–CD powder.

2.3 | Preparation of PCCEs

PVDF and PEG–CDs were dissolved in a mixture of DMF (2 ml) and absolute ethanol (2 ml) by sonication. The content of PEG–CDs was 0–60 wt% of the polymer matrix. The solution was dried in an oven at 80°C for 4 h, and a uniform membrane was obtained in the Teflon container. The membrane was cut into a specific shape and immersed in a commercial electrolyte (1 mol/L of LiPF₆ in EC/DEC/EMC (1:1:1)) overnight.

2.4 | Characterization

X-ray diffraction (XRD) patterns were collected using a Bruker D4 Endeavor X-ray diffractometer with Cu-Ka radiation ($\lambda = 0.1541$ nm, 40 kV). Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Avatar 360 E. S. P. FTIR spectrometer in the range of 4000–400 cm⁻¹ using the KBr pellet method. X-ray photoelectron spectroscopic (XPS) data were obtained using a Thermo ESCALAB 250 electron spectrometer using an Al-Ka X-ray source (1486.6 eV). The morphologies of the samples were observed by scanning electron microscopy (SEM) under a JSM-6390 microscope, while transmission electron microscope (TEM) images of the samples were obtained using a high-resolution TEM (HRTEM) (JEM-2010) at 200 kV.

2.5 | Electrochemical measurements

Symmetric SS/PCCE/SS batteries, SS/PVDF/SS batteries, and SS/LE/SS batteries were assembled to test the ionic conductivity using Equation (1) as follows:

$$\sigma = \frac{L}{RS},\tag{1}$$

where *L*, *R*, and *S* are the thickness, the bulk resistance, and the area of the sample, respectively. The thickness of

PCCEs is about $100-250 \,\mu$ m, and the diameter is 12 mm. The impedance spectrum was recorded in the range of 0.1–100 kHz, while an amplitude voltage of 10 mV was applied. Cyclic voltammetry (CV) at a scan rate of 0.5 mV/s was applied to determine the electrochemical windows of the GPEs in an SS/PCCE/Li battery.

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Symmetric Li/Li batteries were assembled to determine the lithium-ion transference number (t_{Li^+}) from impedance spectra and chronoamperometry. The value of t_{Li^+} was calculated using Equation (2) as follows:

$$t_{\rm Li^+} = \frac{I_{\rm s}(V - I_0 R_0)}{I_0 (V - I_{\rm S} R_{\rm S})},\tag{2}$$

where *V* is the amplitude voltage, I_0 is the initial current, and R_0 is the initial charge-transfer resistance; I_s and R_s are the current and the charge-transfer resistance in the steady state after direct current polarization, respectively.

To prepare positive electrodes, LPF (or $LiCoO_2$), carbon black, and PVDF were dispersed in an N-methylpyrrolidone (NMP) solvent with a weight ratio of 8:1:1. After magnetic stirring for 8 h to obtain a uniform slurry, the obtained slurry was coated onto an aluminum foil and dried at 60°C overnight. The dried electrode was transferred to a vacuum oven and treated at 120°C for 2 days to remove residual NMP. The obtained electrode was cut into discs with a diameter of 16 mm and packed with lithium metal and PCCEs into a battery in an argon-filled glovebox (H_2O , $O_2 < 0.01$ ppm). The galvanostatic charge/discharge cycling tests for Li/Li symmetric batteries were measured at 0.1 and $0.5 \,\mathrm{mA/cm^2}$ with an interval of 1 h. The cycle test was carried out at a rate of 0.5 C for LPF/Li (1 C = 170 mAh/g)and $LiCoO_2/Li$ (1 C = 270 mAh/g). The C-rate tests were performed at a range of 0.2-2 C.

3 | **RESULTS AND DISCUSSION**

CDs synthesized from citric acid and ethylenediamine^{12,13} have high yield, uniform sizes, and abundant functional groups (Figure 1A), which are ideal nanoparticles for crosslinking polymers to form a composite network (Figure 1B). Specifically, the raw materials were dissolved in DMF solution, enclosed in autoclaves, and heated at 170°C for 5 h. The products were precipitated by centrifugation, washed with ethanol, and dried at 80°C. The XRD pattern of the CDs in Supporting Information: Figure S1 has a broad peak centered at 18.3°, indicating a nearly amorphous structure of the obtained brown powder (Supporting Information Figure S2). Under a TEM, these CDs have a uniform size of about 5 nm with a clear lattice distance of 0.21 nm



FIGURE 1 (A) Solvothermal synthesis of CDs from CA and EDA, and the subsequent reaction between CDs and PEG to produce (B) PEG–CDs (DCC and DMAP are 1,3-dicyclohexylcarbodiimide and 4-dimethylaminopyridine, respectively). (C) TEM image of CDs and the inset HRTEM image. (D) TEM image of PEG–CDs and the inset HRTEM image. (E) FTIR spectra of CDs and PEG–CDs. CA, citric acid; CD, carbon dot; EDA, ethylenediamine; FTIR, Fourier transform infrared; HRTEM, high-resolution transmission electron microscope; PEG, polyethylene glycol.

(Figure 1C), which is generally regarded as the graphite lattice.¹⁴ In contrast, the as-prepared PEG-CDs were obtained in the form of a yellow powder (Supporting Information: Figure S2), which appears with a cluster structure in the TEM image (red circles in Figure 1D). In the HRTEM image in the inset, the same graphite lattice distance of 0.21 nm is also observed in PEG-CDs, which indicates that PEG molecules have been connected by CDs to form a large network structure. FTIR spectroscopy was used to characterize the surface groups of the CDs and the PEG-CDs. For CDs, the broad bands between 3500 and 3000 cm⁻¹ correspond to the stretching vibrations of O–H and N–H, respectively,¹⁵ which can be utilized as connection points for PEG. Besides, C-H stretching vibrations at 2926 and 2876 cm⁻¹, CH₂ vibrations at 1465 and $1399 \text{ cm}^{-1,16} \text{ C=O/C=C}$ bonds at 1660 cm^{-1} , and C-N bonds at 1560 cm^{-117} could be observed in the FITR spectrum of the CDs (red line in Figure 1E). After connection with PEG, the FTIR

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spectrum of PEG-CDs (black line in Figure 1E) shows significant changes. First, the FTIR peak intensities of the O-H and N-H vibrations decrease sharply. Second, the typical C–O–C vibration of PEG^{17} at 1100 cm^{-1} is observed in PEG-CDs. Finally, both the C=O vibration of the amide group¹⁸ at 1647 cm⁻¹ and the C=O vibration of the ester group¹⁹ at 1730 cm^{-1} are observed, confirming that the esterification and amide reactions between -OH and -NH₂ groups of the CDs and the -COOH groups of the PEG-COOH molecules have occurred, respectively. It should be mentioned that before crosslinking reactions, PEG molecules were oxidized into PEG-COOH molecules. The FTIR spectrum (Supporting Information: Figure S4) of PEG-COOH shows the typical -COOH vibration at about 1730 cm^{-1} and the C–O–C vibration from PEG at 1100 cm^{-1} .

The elementary composition and structural features of the CDs were analyzed by XPS. Three peaks at 284.0, 399.0, and 530.0 eV are found in the XPS curves of both CDs (Supporting Information: Figure S5A) and PEG-CDs (Supporting Information: Figure S5B), which are attributed to C 1s, N 1s, and O 1s, respectively.²⁰ The CDs contain carbon (65.81%), nitrogen (8.33%), and oxygen (25.86%), obviously different from PEG-CDs. After grafting PEG, the nitrogen content of the CDs reduces from 8.33% to 2.17%, while the contents of carbon and oxygen increase simultaneously. More intuitive changes are found in the high-resolution XPS. The C 1s band of the CDs (Supporting Information:-Figure S5C) and the PEG–CDs (Supporting Information: Figure S5D) can be deconvoluted into four peaks of C=Cat 284.2 eV, C-C at 284.8 eV, C-N/C-O at 286 eV, and C=O at 288 eV. It is observed in the C 1s spectra that the area of C-O/C-N increases, while that of C=C decreases after PEG groups are grafted onto CDs, which is proof of the esterification and acylation between CDs and PEG-COOH molecules. The crystallinity of these two samples is measured by differential scanning calorimetry, and the results are compared in Supporting Information: Figure S6. The melting point (T_m) and the melting enthalpy ($\Delta H_{\rm m}$) decrease from 62.27°C (PEG) to 52.95°C (PEG-CDs) and from 195.8 J/g (PEG) to 157.8 J/g (PEG-CDs), respectively, which means that the amorphous fraction of the polymer increases significantly and this is beneficial for ionic conductivity.²¹

PVDF is widely used as the electrode binder and separator with strong mechanical properties and good thermal stability.²² However, the retention and absorption rate of the PVDF-based electrolytes are always limited because the highly crystallized PVDF chains drastically hinder the ion mobility inside the membrane,²³ which could be improved by introducing additives and blending with other polymers.^{24,25} In the SEM images, the surface morphology of the GPEs membrane has changed considerably after introducing PEG-CDs. When PEG-CDs are absent, the sample surface is flat, with spherocrystal structures of several micrometers, which indicates the crystallization of PVDF chains (Figure 2A). In contrast, the surface morphology of the electrolyte changes drastically after PEG-CDs are added. After introducing 10 wt% PEG-CDs (Figure 2B), the PCCEs show a wrinkled texture on the surface, which may be caused by the crosslink between polymer chains.²⁶ The area of the wrinkled texture and the degree of fold increase gradually when increasingly more PEG-CDs are added (Figure 2C). At the same time, some porous structures are observed on the surface of the membrane when the content of the PEG-CDs reaches 30 wt% (Figure 2D). It has been found that the pore channels on the surface are able to facilitate ion migration and accelerate electrolyte infiltration into the membrane.²⁷ Obviously, the incorporation of PEG-CDs

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led to the creation of a porous network structure for the electrolytes. Furthermore, PEG-CDs can absorb and retain LEs through the polymeric frameworks due to their high affinity with LEs,²⁸ which further increases the ion conductivity. When the content of PEG-CDs reaches 40 wt% (Figure 2E), spherocrystals with a porous structure emerge again, but the spherocrystal sizes are smaller than those in Figure 2A, which reflects the change in the crystallinity of the polymer host.^{11,29,30} Correspondingly, the ionic conductivity of the PCCEs shows a trend of first increasing and then decreasing (Figure 2F). For the PVDF-GPEs without PEG-CDs, the ionic conductivity is rather low $(1.83 \times 10^{-5} \text{ S/cm})$. When the PEG-CDs fraction reaches 30 wt%, the ionic conductivity of the obtained electrolyte increases up to 5.5×10^{-3} S/cm. This value is higher than those of PEGor CDs-incorporated composite electrolytes (Supporting Information: Figure **S7**). For PEG-incorporated samples. the optimal PEG content is 20 wt% ($1.76 \times 10^{-3} \text{ S/cm}$), while the higher PEG content decreases the uniformity and mechanical strength of the membrane. For CDs-incorporated samples, the optimal CD content is 10 wt% (6.63 × 10^{-4} S/cm), while the ionic conductivity of the samples decreases quickly as the CDs content increases continually, indicating that the nanoparticle agglomeration will impede ionic migration. It is clear that the PEG-CDs-incorporated samples perform much better than the above PEG- or CDs-incorporated samples. Even when the PEG-CDs content reaches 40 wt%, the conductivity of the obtained PCCEs is still above 2.5 mS/cm. These results confirm the synergistic effects in PEG-CDs: PEG chains hinder CD aggregation on the one hand, and on the other, CDs enhance the mechanical properties of the polymer electrolytes. The XRD patterns in Figure 2G also confirm the advantages of PEG-CDs over PEG or CDs as fillers. It is well known that PVDF is highly crystalline, with characteristic XRD peaks at 18.86° and 20.77° (green line). These peaks are significantly suppressed after PEG molecules (black line) or CDs (blue line) are incorporated, but still exist in the corresponding XRD patterns. However, after introducing PEG-CDs (red line), the obtained PCCEs are totally amorphous as shown in Figure 2G.

The electrochemical stability windows (ESWs) of the samples were measured by CV scans. The terminal groups influence the ESW significantly. For example, Yang et al.³¹ reported that replacing -OH with $-OCH_3$ could increase the ESW of the electrolytes from 4.0 to 4.3 V. As shown in Figure 2H, for the PEG- or CD-incorporated composite electrolytes, the corresponding ESWs are 3.9 and 4.3 V, respectively. However, PCCEs remain stable until the voltage increases to 4.8 V. The enlarged ESW shows that the combination of PEG



FIGURE 2 SEM images of the PCCEs containing different contents of PEG-CDs: (A) 0 wt%, (B) 10 wt%, (C) 20 wt%, (D) 30 wt%, and (E) 40 wt%, respectively. (F) Ionic conductivity of the PCCEs with different contents of PEG-CDs at room temperature. (G) XRD patterns of PVDF, CD-incorporated GPEs, PEG-incorporated GPEs, and PCCEs, respectively. (H) The electrochemical windows for PCCEs. (I) A PVDF film and a PCCE film. (J-L) Folding, wrapping, and recovering tests of PCCEs. Photos of the commercial separator and the PCCEs with different contents of PEG-CDs (M) at 25°C and (N) after heating at 200°C for 2 h, respectively. CD, carbon dot; EDA, ethylenediamine; GPE, gel polymer electrolyte; PCCE, PEG-CD composite electrolytes; PEG, polyethylene glycol; PVDF, polyvinylidene fluoride; SEM, scanning electron microscope; XRD, X-ray diffraction.

and CDs can effectively decrease the activity of the terminal group of CDs^{32,33} and also improve the oxidation-resistance ability of PEG.34,35

Figure 2I-L shows photos of these samples. After incorporation of PEG-CDs, the color of the PVDF film changes to yellow, consistent with the color of the PEG-CDs powder. After repeated folding and wrapping, the PCCEs films recover to the original shape, indicating their good flexibility and stability. Energy-dispersive X-ray spectroscopy (EDS) is used to study the element dispersion of the PCCEs. As shown in Supporting Information: Figure S8, the EDS mappings of P and N show the homogeneous distribution of LiPF₆ and PEG-CDs, respectively. Such evenly distributed additives and lithium salts are beneficial for achieving a continuous amorphous structure as well as good stability of the membrane.³⁰ When preparing GPEs for LMBs, the polymer hosts lose some mechanical properties after absorbing solvents. To solve this problem, we designed a cross-linked network structure with uniformly distributed CDs for GPEs to improve the mechanical properties. After PEG-CDs are distributed homogeneously in GPEs, the obtained polymer-nanoparticle network confers the membrane with a good tensile property. In Supporting Information: Figure S9A, the PCCEs and PVDF-GPE membranes are cut into the same shape for stress-strain testing. The maximal tensile strength of PCCEs is measured to be 21.3 MPa, which is much higher than that of PVDF-GPEs (15.2 MPa). Also, the PCCEs show an excellent tensile property with the elongation of 1445% at break, about three times that of PVDF-GPEs (470%). Moreover, the dense network of PEG-CDs is able

to enhance the elasticity of the membrane. Supporting Information: Figure S9B shows the elasticity modulus of the electrolyte films. When the indentation depth is 1100 nm for both samples, the load on PCCEs is 1.5 mN and that on PVDF-GPEs is 0.6 mN, indicating that PCCEs are softer than PVDF-GPEs. Such a soft electrolyte facilitates contact between the electrode and the electrolyte, so the interface impedance can be reduced. Thermal stability is another important parameter of the electrolytes because thermal shrinkage and melt of the polymer electrolytes will cause a short circuit inside the battery and even trigger safety accidents.⁵² The TGA profiles of PVDF GPEs, PCCE films, and commercial separators (mainly polyolefin) are compared in Supporting Information: -Figure S10. After heating at 200°C for 2 h, the commercial separator melts completely and the PVDF GPEs shrink to small pieces. On the contrary, the more the PEG-CDs incorporation, the fewer the changes observed in PCCEs (Figure 2M,N). When the PEG–CDs content is increased to 30 wt%, the as-prepared PCCEs can retain the original shape and still work in batteries. Such a remarkable improvement in thermal stability by the PCCEs could be attributed to the thermostability of the rigid CDs themselves⁵³ and the three-dimensional polymeric framework that remains stable at high temperatures.⁵⁴

The role of PEG-CDs in PCCEs can be illustrated by a scheme, as shown in Figure 3A. First, PEG chains prevent CDs from agglomerating so as to achieve a homogeneous distribution of the filler. Such welldispersed CDs can effectively promote the dissociation of lithium salts¹¹ and reduce the crystallinity of the polymer host. As a result, the incorporation of PEG-CDs improves the ionic conductivity of the PCCEs. The ion transference number (t_{Li^+}) was measured by chronoamperometry and electrochemical impedance spectroscopy (EIS) with an applied potential of 10 mV before and after polarization (Figure 3B,C). Equivalent circuits for impedance spectra were fitted and are shown in Supporting Information: Figure S11, and the t_{Li^+} of the symmetric battery using LEs is 0.24, while that of the battery with PCCEs as electrolytes boosts up to 0.71 (Supporting Information: Table S1). A higher t_{Li^+} decreases the concentration polarization inside the battery and promotes Li⁺ migration, which is beneficial for the homogeneous deposition of the Li⁺. The higher t_{Li^+} of our PCCEs can be ascribed to the following reasons. First, the intermolecular interaction among lithium salts, PEG-CDs, and PVDF can restrain the movement of the anions. Comparing the FTIR spectra of the PCCE membrane before and after absorption of LEs (Supporting Information: Figure S12), the $-CH_2$ - bending vibration³⁶ shifts from 1403 to 1404 cm⁻¹ and the CH shifts from 2932 to 2934 cm^{-1} , respectively, which

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indicates that the H–F hydrogen bonds between PF_6^- and PVDF chains or PEG–CDs can restrict the movements of the anions.³⁷ Meanwhile, numerous polymeric chains form dense networks that restrain the motion of anions with large sizes in PCCEs due to the volume effect.³⁸ On the contrary, smaller and disassociated Li⁺ can pass through the dense network structure with an improved t_{Li^+} .

Li/Li symmetric batteries are also assembled for plating-stripping experiments to study the stability of electrolytes. When bare CDs fillers are added in the electrolytes, the polarization increases significantly after 310 h of galvanostatic cycling at a current density of 0.1 mA/cm² with an interval of 1 h in each cycle (Supporting Information: Figure S13), which indicates that the surface groups of CDs have high reactivity with lithium electrodes. On the contrary, the symmetric battery with PCCEs as electrolytes can be operated steadily for more than 3500 h (Supporting Information: Figure S14) without obvious polarization or short circuit under the same testing conditions. The voltage of the Li/ PVDF-GPEs/Li decreases sharply after 800 h cycling and becomes very low, which is caused by a short circuit inside the battery. Also, the short circuit occurs after 1200 h cycling for the symmetric battery with LEs. In terms of the overpotential, Li/PCCE/Li has a lower overpotential than that of Li/PVDF-GPE/Li throughout the testing process, but higher overpotential than that of Li/LEs/Li due to the commercial ultrathin separator film. At a larger current density of 0.5 mA/cm², the PCCEsbased symmetric battery also shows the best cyclic stability among three symmetric batteries, which remained stable for over 1400 h. Furthermore, its overpotential is slightly below 100 mV and shows tiny potential polarization during the cycling tests (Figure 3D). In contrast, the PVDF-based symmetric battery showed drastic voltage fluctuations, and the commercial LE-based symmetric battery developed a short circuit after 200 h cycling. These lithium plates, after cycling, are taken out and observed by SEM to study the status of the ion deposition by SEM (Supporting Information: Figure S15). It can be found that the lithium plate surface from Li/PCCEs/Li is smooth and dense, without any dendrites or dead Li. On the contrary, the surfaces of Li plates from PVDF-GPE- and LE-based batteries show many stacks of voids and particles. The accumulation of such uneven lithium deposition will result in the formation of dendrites and even short circuit, and finally adversely impact the cycling performance and the safety of batteries.³⁹ The above obvious discrepancy indicates that PCCEs are able to facilitate lithium deposition safely and prevent the formation of lithium dendrites. Moreover, Li/PCCEs/Li can also operate at a high current



FIGURE 3 (A) Schematic working mechanisms for the PCCEs in improving ion conductivity and the ion transference number. Ion transference number measurements of symmetric batteries using (B) LEs and (C) PCCEs as electrolytes, respectively. (D) Galvanostatic cycling tests of Li/Li symmetric batteries using LEs, PVDF–GPEs, and PCCEs, respectively, at the same current density of 0.5 mA/cm². CD, carbon dot; GPE, gel polymer electrolyte; LE, liquid electrolyte; PCCE, PEG–CD composite electrolytes; PEG, polyethylene glycol; PVDF, polyvinylidene fluoride.

density of 2 mA/cm^2 for 2 mAh/cm^2 per cycle, and the results are shown in Supporting Information: Figure S16. This symmetrical cell using ultra-thin PCCEs showed an extremely low overpotential within 63 mV even after 500 h, which confirms the ability of PCCEs to suppress lithium dendrites at high current densities.

The performance of PCCEs is also tested in LPF/Li metal batteries for comparison with PVDF–GPEs and LEs. The initial discharge capacity of LPF/PCCEs/Li is 143 mAh/g at 0.5 C, and the corresponding Coulombic

efficiency reaches 90.63%, which is lower than the performance of LPF/LEs/Li (161.1 mAh/g, 95.55%), but higher than those of LPF/PVDF–GPEs/Li (139.7 mAh/g, 94.5%; Figure 4A). Nevertheless, LPF/PCCEs/Li shows the best results in specific capacities and capacity retention rates. After the first 200 cycles, the LPF/PCCEs/Li shows almost no fading capacity, and its discharge capacity remains at 99.86% of the initial discharge capacity. Moreover, its capacity retention rate still remains 96.02% after 300 cycles. In contrast, the

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FIGURE 4 (A) Discharge capacity and Coulombic efficiency of three LiFePO₄/Li batteries at 0.5 C, using LEs, PVDF–GPEs, and PCCEs as electrolytes, respectively. (B) The corresponding discharge capacities of the above batteries at the 1st, 100th, 200th, and 300th cycle, respectively. (C) LiFePO₄/PCCEs/Li battery cycling performance at 2 C. (D) The rate performance of three batteries with different electrolytes. (E) Voltage profiles of LiFePO₄/PCCEs/Li battery at different rates. (F) SEM image of the Li anode before cycling. SEM images of the Li anode plates after 90 cycles at 0.5 C from (G) LiFePO₄/LEs/Li, (H) LiFePO₄/PVDF–GPEs/Li, and (I) LiFePO₄/PCCEs/Li batteries. CDs, carbon dots; GPE, gel polymer electrolyte; LEs, liquid electrolytes; PCCEs, PEG–CDs composite electrolytes; PEG, polyethylene glycol; PVDF, polyvinylidene fluoride; SEM, scanning electron microscopy.

capacity of LPF/LEs/Li deteriorates drastically and drops to 131 mAh/g after only 100 cycles, and eventually stabilizes at around 120 mAh/g. The performance of LPF/PVDF-GPEs/Li is even worse. Its discharge capacities at each stage (100, 200, and 300 cycles) are obviously lower than those of LPF/PCCEs/Li, as shown in Figure 4B. For comparison, another GPE was prepared by blending PVDF and poly(ethylene oxide) (PEO), and then soaking in a LE. Such a PVDF-PEO-GPE was also assembled in an LFP battery for cycling tests (see Supporting Information: Figure S17), which shows an excellent cycling property during the first 200 cycles (137.6 mAh/g, 99.15%), but its capacity and Coulombic efficiency showed an obvious decrease after 280 cycles (118 mAh/g, 94.23%). When these three kinds of electrolytes are assembled in LiCoO₂/Li metal batteries, the disparity between them becomes even larger (Supporting Information: Figure S18). The LiCoO₂/PCCEs/Li battery shows an initial discharge capacity of 150.7 mAh/g and a stable value of 127 mAh/g after 350 cycles. The capacity of the LiCoO₂/LEs/Li battery decreases continuously, and there is about only half of the initial capacity left after 150 cycles. The LiCoO₂/PVDF-GPE/Li battery performs worse, which does not retain a long lifespan over 300 cycles. The above differences in the discharge capacity of three batteries are compared (Supporting Information: Figure S18) at the 100th, 200th, and 300th cycle, respectively. The LPF/PCCEs/Li battery is operated at various current densities to simulate practical applications (Supporting Information: Figure S19). After cycling at different rates and then reverting to the initial current density (0.2 C), the battery still has a discharge capacity of 162.4 mAh/g, and both the capacity retention and the Coulombic efficiency are close to 100%. Furthermore, the battery shows a stabilized discharge capacity of 124.5 mAh/g at 2 C and an outstanding stability with a high Coulombic efficiency of 99.37% after 900 cycles, as shown in Figure 4C. In general, the rate performance of the LPF/Li battery is usually evaluated by tests at different C-rates ranging from 0.2 to 2C(1C = 170 mA/g) at room

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temperature. As a control, the capacity of LPF/ PVDF-GPE/Li decays radically on cycling at a high rate. Specifically, when the rate increases to 2 C, the capacity of LPF/PVDF-GPE/Li is only 33.4 mAh/g, because the low ionic conductivity and the large interfacial impedance limit ion migration. In contrast, LPF/PCCEs/Li delivers discharge capacities of 134.7 mAh/g at 1 C and 120.6 mAh/g at 2 C, respectively. These results even exceed those of LPF/LEs/Li, with discharge capacities of only 128.8 mAh/g at 1 C and 98.4 mAh/g at 2 C, respectively. In addition, the discharge voltage plateaus of the LPF/PCCE/Li battery are located at 3.39, 3.33, 3.31, and 3.26 V versus Li/Li^+ (Figure 4E), which are consistent with the standard values of LPF.⁴⁰ The above high cycling stability and rate capability benefit from the network structure⁴¹ of PCCEs and ion-conducting polymer brushes⁴² added to CDs. Supporting Information: Tables S2 and S3 show objective comparisons of our PCCEs with other previously reported GPEs containing PEG and some PEO-based electrolytes, respectively. It is clear that our PCCEs have excellent conductivity, good transference number, and enough ESW for use as composite electrolytes. Furthermore, when assembled in LMB, our battery shows excellent cycling properties at room temperature. Since CDs with abundant groups are ideal crosslinkers to construct polymeric networks and no further modification or postprocessing of the as-prepared polymer electrolyte is needed, the low cost and easy processing of our LPF/PCCEs/Li battery make it more practical in applications.

The CV curves of the LPF/PCCEs/Li battery were tested at a scan rate of 0.5 mV/s (Supporting Information: Figure S20). The oxidation and reduction potentials of the battery are located at 3.85 and 3.12 V in the first cycle, respectively. After four cycles, the oxidation potential increases to 3.91 V and the reduction potential decreases to 3.10 V, because of the formation of a solid electrolyte interface (SEI) film between the electrode and the electrolyte. The SEM image of the crosssectional picture for the lithium plate from the LPF/ PCCEs/Li (Figure 5A) shows a clear SEI layer on the electrode surface after 90 cycles. It is well known that a dense and uniform SEI can effectively prevent the side reactions between the electrode and the electrolyte and suppress dendrite growth, so as to improve the cycling performance of the battery.^{43,44} Energy-dispersive X-ray spectroscopy is used to investigate the surface composition and elemental distribution of the SEI. The result shows that after 90 cycles, the Li plate surface mainly contains four elements, including carbon, oxygen, fluorine, and phosphorus (Figure 5A). The distributions of these elements are homogeneous and continuous, confirming the uniformity of the SEI layer.45 The

composition and valence of the SEI layers from different batteries are further investigated by XPS. For the LMB using LEs, the C-C (284.6 eV), COR (286.6 eV), and CO_3^{2-} (290.2 eV) groups in the C 1s spectrum (Figure 5B) could be attributed to the decomposition of liquid solvents and lithium salts, which can be further confirmed by the F 1s spectrum. In Figure 5C, C-F (686.4 eV), LiF (685.6 eV), and $Li_r PO_v F_z$ (687.4 eV) can be seen and these can be regarded as the reduction products of LiPF₆ and solvents. These results indicate that the LEs-derived SEI layers contain many inorganic constituents, which could not inhibit lithium dendrites, resulting in inferior cyclic performance of the battery.⁴⁶ For the LMBs using PCCEs as electrolytes, the compositions of the obtained SEI layers are significantly different. Besides the C-C and C=C groups shown in the C 1s spectra, COOR (288 eV), and C-O/C-N (286 eV) groups can also be seen in Figure 5D. Since PEG-CDs contain N and PVDF contains F, these elements are also detected in SEI by XPS. In particular, in Figure 5E, the peaks at 688.4 eV are assigned to the -CH₂CF₂- of the PVDF from the PCCEs. Both the C 1s and F 1s spectra confirm that PCCEs are involved in SEI formation, which can reduce the decomposition of other components inside the battery.⁴⁷ It is reported that the -CH₂CH₂O- unit pined into the polymeric networks regulates the migration of lithium ions and shows strong interactions with other components, thus enhancing the stability of the SEI layers.⁴⁸ Also, PVDF chains can effectively coat the surface of the lithium plate and promote the formation of flexible polymer layers with other products.^{30,49,50} Another important difference between Figure 5C, E is that the former has no $LiPF_6$ signal at 689.4 eV, while the latter shows the presence of a considerable amount of LiPF₆ in the PCCEs-derived SEI layer. This phenomenon indicates that LiPF₆ has decomposed on the Li anode surface in LPF/LEs/Li during cycles, which adversely affects the whole battery. As proof, the decomposition product LiF is present in large amounts, as can be seen in Figure 5C, while the LiF content in the SEI of LPF/PCCEs/Li is negligible. In addition, the ionic conductivity of $Li_x PO_v F_z$ is much higher than that of LiF,⁵¹ which contributes to a higher ion conductivity of the SEI of LPF/PCCEs/Li. EIS spectra of the LPF/Li batteries during the cycling measurements further confirm the above issues. In Supporting Information: Figure S21, the impendence of LPF/LEs/Li increases continuously due to the unstable SEI layers. On the contrary, although the impendence of LPF/PCCEs/Li increases gradually over 10 cycles, it becomes stable in the following cycles. Obviously, a robust, conductive, and stable SEI layer has been established between the lithium anode and PCCEs,



FIGURE 5 (A) Cross-sectional SEM image of the Li deposition layer on the Li anode of a LiFePO₄/PCCE/Li battery after 90 cycles and the corresponding EDS mapping. XPS spectra of (B and D) C 1s and (C and E) F 1s of the Li deposition layers from LiFePO₄/LE/Li and LiFePO₄/PCCE/Li batteries after 90 cycles, respectively. CD, carbon dot; EDS, energy-dispersive X-ray spectroscopy; LE, liquid electrolyte; PCCE, PEG–CD composite electrolytes; PEG, polyethylene glycol; SEM, scanning electron microscopy; XPS, X-ray photoelectron spectroscopic.

which promotes homogeneous deposition of lithium and prevents the decomposition of lithium salts.

4 | CONCLUSION

A crosslinked PEG–CD network has been obtained from the chemical reactions between PEG and CDs under the catalysis of DCC/DMAP. After incorporating PVDF and LEs, a composite electrolyte with outstanding performance is obtained. The PEG–CDs not only reduce the crystallinity of the PVDF matrix, yielding continuous amorphous conductive regions, but also provide a stable framework with good mechanical, thermal, and electrochemical properties. Furthermore, such PCCEs have high ion transference numbers and promote the formation of stable SEI, which promotes homogeneous ion deposition on the anode and inhibits lithium dendrite simultaneously. During long cycles at room temperature, both LPF/PCCE/Li and LiCoO₂/PCCE/Li batteries show much better cycling stability and retention rate than the control LMB with PVDF–GPEs and LEs, respectively. The good

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performance and low cost of PCCEs make them promising candidates as the GPEs/separator for future LMBs.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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