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Single Li ion conducting solid-state polymer electrolytes based on poly(lithium 4-styrene sulfonate) and citric acid carbon quantum dots for Li-metal batteries

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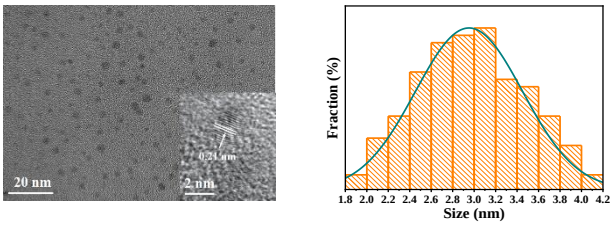
Zeyu Li[1], Yu Li[1], Yiyu Feng[1,2], Wei Feng[1,2]*

[1]*School of Materials Science and Engineering, Tianjin University, China*
[2]*Key Laboratory of Advanced Ceramics and Machining Technology Ministry of Education, China*

Introduction

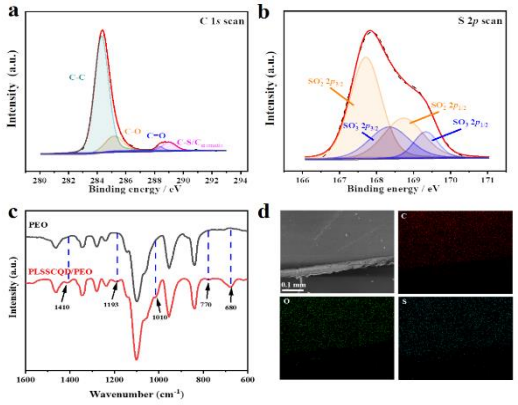
Single Li ion-conducting solid-state polymer electrolytes (SLIC-SPEs) can effectively inhibit the growth of Li dendrites in Li-metal batteries. However, SLIC-SPE synthesis using traditional polymerization methods yields electrolytes with insufficient conductivity, which limits their practical application. Herein, a novel Li salt based on carbon quantum dots (CQDs) is fabricated via the pyrolysis of poly(lithium 4-styrene sulfonate) and citric acid. The large CQD anionic size hinders anion migration in the polyethylene oxide matrix and thereby grants a high Li+ transport number of 0.9446. Moreover, CQD incorporation improves the mechanical properties and ionic conductivity of the SPEs. All-solid-state Li-metal batteries fabricated with these SPEs show good cycling stability, rate performance, and capacity retention over 1000 cycles at 2 C and 60°C.



a) TEM image of PSSCQD and inset: HRTEM lattice fringe image. b) Size distribution of PLSSCQD particles

TEM studies: The anions are CQDs with diameters of 1.8–4.2 nm, exceeding those of traditional anions by ~10× (the effective radii of typical diffusing species are 0.229–0.402 nm). The HRTEM image (inset of Fig. a) of the CQDs displayed identical and well-resolved lattice fringes, with an interplanar spacing of 0.21 nm corresponding to the (100) facet of graphene carbon.

Characterization of PLSSCQD



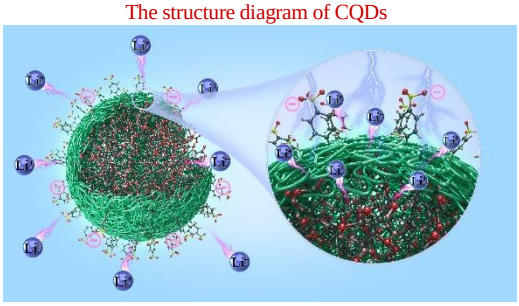
XPS spectra of PLSSCQD in the energy range of a) C 1s and b) S 2p signal. c) FTIR spectra of PEO and PLSSCQD/PEO. d)SEM image of PLSSCQD-4/PEO membrane, and EDS mapping of C, O, and S.

XPS was utilized to measure the elemental composition and the chemical state of CQDs. The CQDs contained 31.06 at% carbon, 64.08 at% oxygen, and 4.86 at% sulfur. Analogous results were demonstrated in the EDS. The high-resolution C1s XPS spectrum can be resolved into four peaks, which are assigned to sp2 carbon atoms (284.4 eV), alcoholic species (C–O, 285.3 eV), carbonyl species (C=O, 288.4 eV), and C–S/Caromatic (289.1 eV). The XPS results further confirmed the presence of the sulfonate anions ($–SO_3^–$) are anchored to pendant group on the polymer around CQD core.

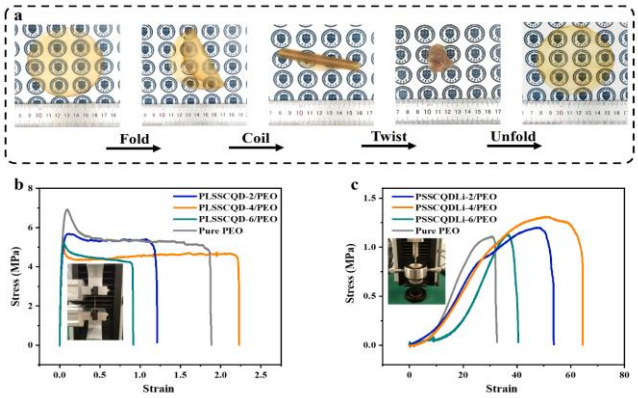
Conclusions

1. A new approach to fabricate SLIC-SPEs based on CQDs was reported.
2. Addition of PLSSCQD ensured superior stretching and puncture resistance properties of SPE.
3. PLSSCQD/PEO SPE exhibited a high room-temperature ion conductivity and Li^+ transport number of 2.02×10^{-4} S·cm^{-1} and 0.9446, respectively.
4. The cell using PLSSCQD/PEO SPE exhibited a dendrite-free morphology during repeated discharge–charge, excellent cycling stability and capacity retention.

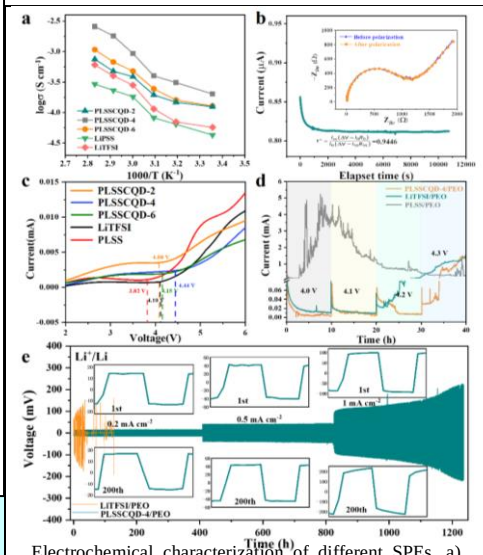
The structure diagram of CQDs



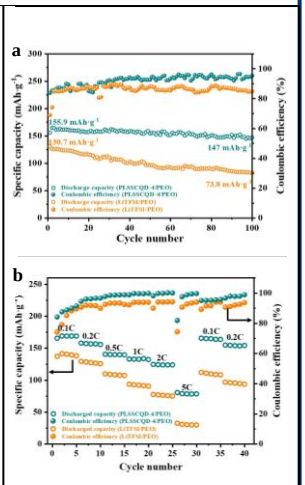
Steric hindrance from the large size of CQDs means that these anions are effectively fixed in the polymer matrix, thereby realizing single Li^+ transport.



Mechanical properties of the prepared membranes. a) Photographs of PLSSCQD-4/PEO SPE film before and after folding, coiling, twisting, and unfolding. b) Tensile stress–strain curves of different membranes. Inset: photo of stretched sample. c) Puncture-resistance stress–strain curves of different membranes. Inset: photo of punctured sample.



Electrochemical characterization of different SPEs. a) Temperature dependent δLi^+ of SPEs from 25 to 80 ° C. b) Chronoamperometry profiles and AC impedance spectra before and after polarization for symmetric Li cells with PLSSCQD-4/PEO at 60 °C. c) LSV of PLSSCQD/PEO, PLSS/PEO, and LiTFSI/PEO electrolytes at a sweep rate of 1 mV·s^{-1}. d) Electrochemical floating analysis of PLSSCQD-4/PEO, LiTFSI/PEO, and PLSS/PEO using NCM523 cathode. e) Galvanostatic cycling for electrolytes in symmetric Li cells at 0.2, 0.5, and 1 mA·cm^{-2} and 60 °C.



Discharge–charge profiles of LFP|SPE|Li cells: a) Capacity and columbic efficiency versus cycle number of the cells at 0.2 C and 60 °C. b) Rate capacities of batteries with different SPEs at 60 °C.

*Contact: weifeng@tju.edu.cn