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PERSPECTIVE ARTICLE

# Polymer derived SiOC and SiCN ceramics for electrochemical energy storage: A perspective

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**Abstract**

Polymer-derived ceramic (PDC) materials with tunable electrochemical properties are at the core of emerging energy storage systems. Applications encompass the development of PDCs as electrodes in both batteries and supercapacitors. This perspective highlights new opportunities for electrode material designs, the importance of PDC material design and integration, and the complexities of realistic PDC applications.

KEYWORDS

energy storage, materials design, metal-ion battery, polymer derived ceramics, testing

## 1 | INTRODUCTION

Energy storage technologies are critical in the sense that they are used to power an application, such as electronic devices, electric vehicles, or electric grid energy storage systems. Electrochemical energy devices utilize reversible energy storage, in which chemical energy is converted into electrical energy and vice-versa and then repeated hundreds or thousands of times. Beyond traditional lithium-ion technology, a new generation of affordable, innovative, and lightweight battery systems will find their way into the ever-advancing era of cellphones, tablets, and laptops. Electric vehicles are going to replace the fuel power with batteries and supercapacitors to achieve better distance/amount of energy, resulting in cost-effective driving. Powerful batteries will completely revolutionize grid energy storage (e.g., customizable microgrids), and may permanently change the fundamental operation of the energy supply system.

However, these ground-breaking innovations require high-performance, low-cost energy storage technologies. Following the replacement of fossil fuels with wind, solar, and stored energy, traditional lithium technologies must evolve to include electrode materials with exceptional properties as well as other charged alkali ions. Researchers have demonstrated how ceramics that are derived from polymeric precursors can provide the necessary boost toward the next-generation electrochemical energy storage.

In the early 1960s, an unusual polymer-to-ceramic conversion was used to develop silicon-based ceramic from organosilicon polymers that were denoted as polymer-derived ceramics (PDCs). Small-diameter silicon carbide-based ceramic fibers were produced, practical application of this ceramic processing route via thermolysis.[1] Notable examples of polymer-to-ceramic transformation technology include films/coatings, fibers, bulk ceramics, and non-oxide ceramics, which are all synthesized with tailored properties.

PDCs offer high thermodynamic/chemical stability against electrochemical corrosion, good mechanical strength, tunable electrical conductivity and porosity and multiple sites in PDC microstructure for reversible alkali metal ion storage, which qualify them as exceptional electrodes for electrochemical storage systems. Depending on the application, PDCs can be shaped into any desirable morphology, size, and structure, making them viable even for textile/wearable energy storage devices. On the other hand, it is nearly impossible to acquire a high-performance electrode from just a single class of material as most have only one or a few of the desired properties. Although PDCs with tailored properties can be used in existing batteries and supercapacitors, efficiency, manufacturing costs, and long-term reliability are essential criteria for investing in and developing PDC technologies.

## 2 | PDCs FOR ENERGY STORAGE

PDC research from the 1960s to 1990s focused on high-temperature applications and ceramics matrix composites, due to PDCs' remarkable thermodynamic stability and high resistance to corrosion and creep. Consideration of PDCs as electrode materials did not commence until the late 1990s.[2] Modification of the final ceramic properties by tailoring processing parameters made PDCs highly desirable for energy storage. Especially, the novel physical and chemical properties of PDCs and their high surface areas and ability to cycle alkali metal ions make them extraordinary electrodes for rechargeable batteries. To this end, PDC materials as active electrode materials are heavily investigated in current state-of-the-art lithium- and sodium-ion cells while some reports on the use of PDC-based electrodes for supercapacitors have emerged recently.

Depending on the pyrolysis temperature PDC can be semiconducting or insulating, which also controls the microstructure and continuous network of an electron conducting region in the pyrolyzed ceramic. The conductivity of a PDC material predominantly corresponds to the amount of free carbon phase in the structure, which typically increases with the rising pyrolysis temperature. Semiconducting to metallic conductivities can be achieved for PDCs pyrolyzed at temperatures of 1000–1400°C. Elemental doping (e.g., B or Al in SiCN) also helps increase the electrical conductivity.[3] Si-based carbon-rich PDCs have demonstrated favorable performances as electrodes for electrochemical energy storage systems.

PDCs can reversibly store lithium up to 900 mAh $g^{-1}$ capacity within the voltage range of 0.0–2.5 V versus $Li/Li^+$ while providing >99% overall coulombic efficiency. However, >25% first cycle loss depending on the PDC composition as well as a voltage hysteresis of 0.8–1.2 V are some of the concerns that still require attention.[4] Altering the molecular structure of the polymer precursor as well as incorporating conducting nanofillers in pyrolyzed ceramic have been shown to mitigate some of these complications. In addition to lithium-ion batteries, PDC-based electrodes have been studied for sodium-ion batteries (SIBs) as well especially PDC-derived hard carbons, which have been proposed as suitable electrodes for SIBs.

Research on supercapacitors is mainly driven by the need for higher power density, which traditional batteries are unable to meet.[7] As shown in Figure 1C, the charge is stored at or near the surface of the electrode material, and because supercapacitors are typically not restricted by the kinetics of ionic diffusion, they can run for a large number of cycles (~$10^6$) at a high charge/discharge current rate. Therefore, a suitable electrode material (with high ionic and electronic conductivity) is essential for the efficient performance of a supercapacitor. PDC-based electrodes, where the silica nanodomains can be etched away resulting in a highly porous carbonaceous material, hold great potential in use as electrodes for an electrochemical double-layer capacitor.

## 3 | MATERIAL DESIGN

One key feature of PDCs is that the traditional low-cost polymer-forming methods such as hot/cold pressing, extrusion, and injection molding may be utilized to fabricate complex ceramic parts upon pyrolysis. Simple and direct polymer-to-ceramic fabrication can process complex structures such as 1D fibers, 2D films/coatings, and 3D shell/core nanocomposites. The PDC approach controls the molecular structures of final ceramic products at molecular/atomic levels and achieves uniformly distributed microstructures. Tailoring processing conditions such as incorporating doping elements, altering polymer composition, varying pyrolysis parameters (temperature, atmosphere, etc.), or utilizing distinct processing techniques such as templating, etching, blowing, decomposition, aerogels, and spinning influence the intrinsic porosity of PDCs.[8]

Several fabrication techniques have been systematically used to incorporate PDC electrodes into batteries and supercapacitors. Figure 2 shows various components and fabrication methods for PDC electrodes. Bulk PDCs-based films (several micrometers thick) have been investigated as electrodes using a tape-casting method. In this process, slurries of PDC powders (usually with other additives) dissolved in an organic solvent are blade-cast onto a current collector film, that is dried and used as an electrode. However, depositing thinner films of PDC precursor and then pyrolyzing the film may increase cycling stability over a bulk powder-based PDC electrode.[9] To achieve a thin film electrode, the utilization of a liquid-spray injector has been proposed. In this technique, using a pulsed liquid injector the liquid polymer precursor is sprayed

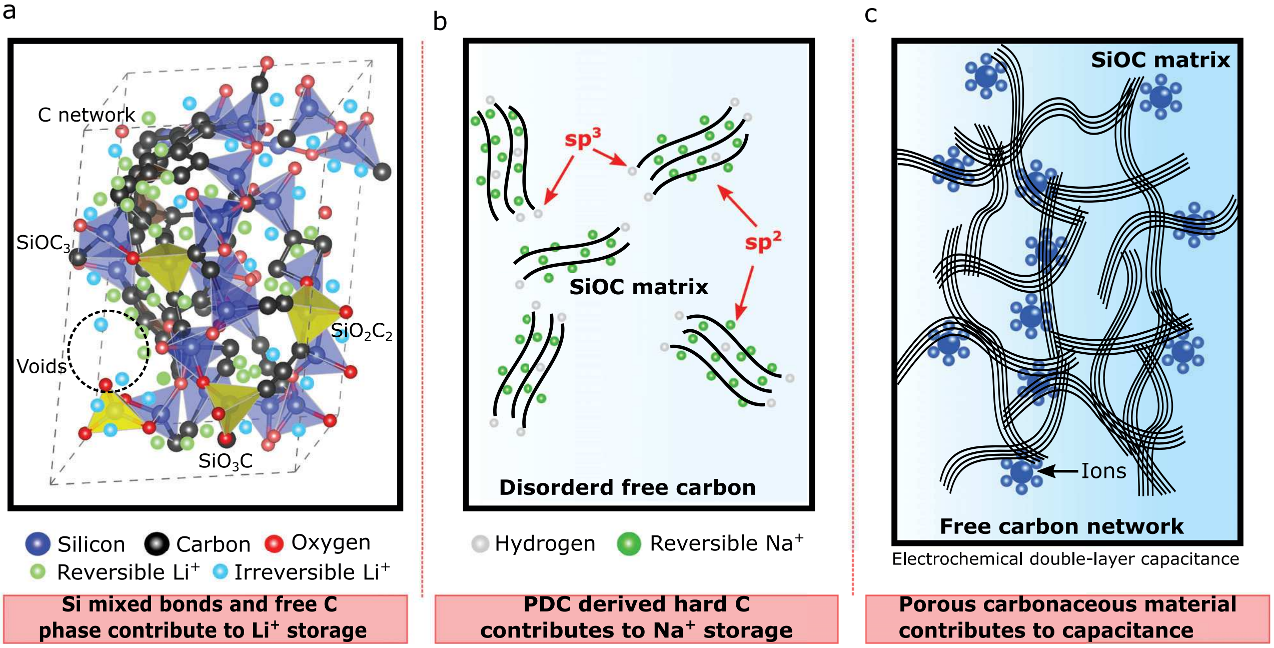

**FIGURE 1** Charge storage mechanism of PDC electrodes in alkali-ion batteries and supercapacitors. (A) The atomic model of silicon oxycarbide (SiOC) ceramic and representation of reversible and irreversible alkali-metal ions storage in the ceramic. The unit cell of SiOC consists of the free carbon phase, $SiO_xC_{4-x}$ units, and nano-voids. The green spheres represent the alkali ions stored reversibly, whereas the blue spheres represent irreversibly captured ions. Reproduced with permission.[5] Copyright 2017 American Chemical Society. (B) Schematic shows likely charge storage mechanism of PDCs in Na-ion batteries (SIBs). (c) In an electrochemical double-layer capacitor (EDLC), ions adsorption occurs at the electrode surface of the free carbon network derived from PDCs. Reproduced with permission.[6] Copyright 2020 Elsevier B.V

onto a metal current-collector substrate and pyrolyzed into ceramic for electrochemical cell fabrication. Such electrodes are free from additives (binders, solvents, etc.), which reduces the overall weight of the assembled cells. On the other hand, additive manufacturing beneficially exploits the processing flexibility and hierarchical porosity of PDC precursors. Using 3D printing technology, complex PDC ceramic has been fabricated by direct ink writing from a precursor containing ink with suitable rheology. In another additive manufacturing-based technique, UV/laser lithography has been employed to fabricate the complex 3D structure of PDC. In this technique, photosensitive liquid preceramic resins are used, where the UV/laser power can be controlled as well as the exposure dose and time to manipulate the final ceramic structure. Last, electrospinning of preceramic polymers has been utilized to prepare flexible cloth-like electrodes upon pyrolysis (consisting of non-woven nanometer-size hollow fibers of PDC) for batteries and supercapacitors to achieve outstanding electrochemical performance. The hierarchical porous structure along with the core-shell structure of the flexible fiber mat electrode provides additional sites for ion storage and can effectively buffer volume changes associated with ion insertion/extraction upon successive cycling.

## 4 | CHALLENGES AND OPPORTUNITIES OF PDCs IN CURRENT ELECTROCHEMICAL ENERGY STORAGE SYSTEMS

Present-day electrochemical energy devices continue to experience fundamental problems that must be resolved before such devices can utilize their full potential. Among them, electrode decomposition is a significant factor that limits the usability of rechargeable metal-ion batteries. Specifically, when the oxidative range of the electrolyte is surpassed beyond the usual limit, the positive electrode begins to disintegrate, which decreases cell life.[10] Continuous intercalation/deintercalation during cycling leads to several side reactions at both electrodes, allowing faster decomposition of the electrode. This irreversible loss of active material volume results in capacity difference and increasing capacity fading. PDCs may offer a remedy to this problem as they are mechanically and chemically stable for a large number of cycles.

Formation of a solid–electrolyte interface (SEI) passivation layer on the anode surface is an important issue that is constantly encountered.[11] The SEI generally forms due to the intercalation of alkali metal ions at the electrode surface, resulting in the irreversible consumption of ions

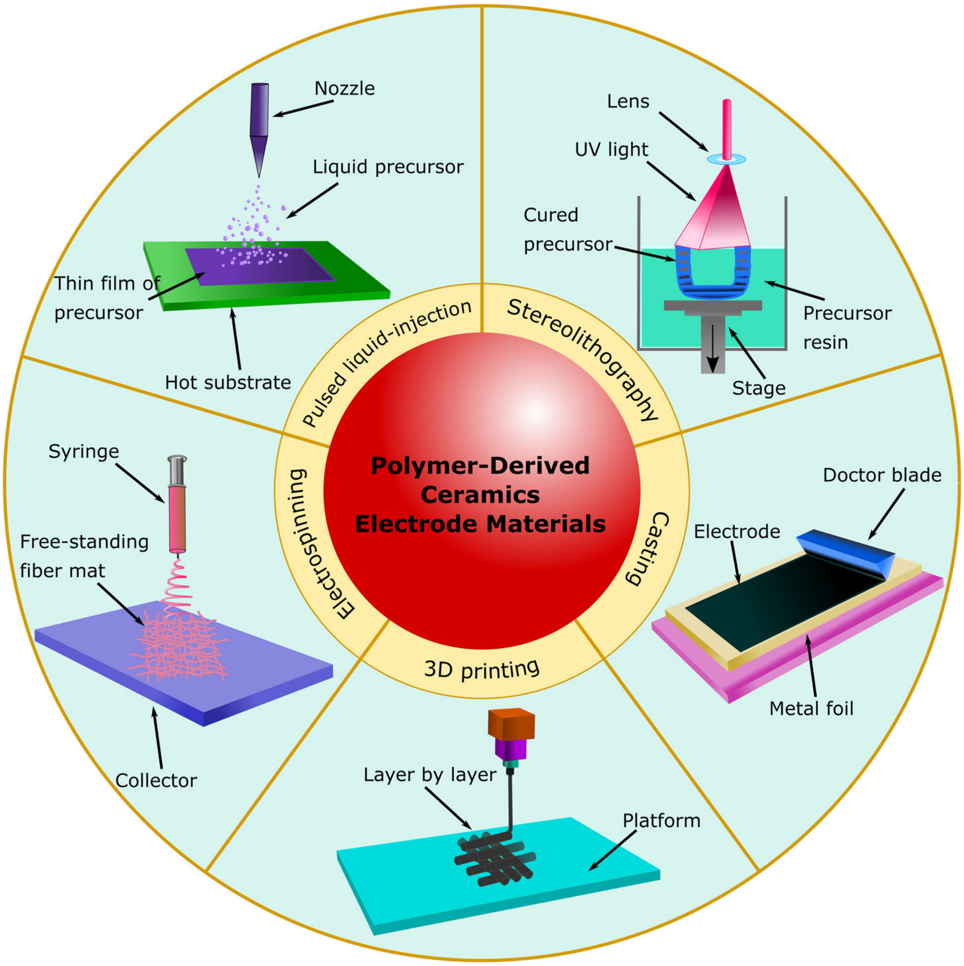

**FIGURE 2** Schematic illustration of the different techniques that have been employed to fabricate PDC electrodes for electrochemical energy storage systems

from the electrolyte, especially in the first few cycles to accommodate ion diffusion-related volume change. However, the formation of a passivation layer may also deter further degradation of the electrolyte in successive cycles as long as the mechanical integrity of the SEI is maintained. PDC-based materials because of their superior thermodynamic stability and resistance to electrochemical corrosion against various electrolytes may offer protection against parasitic reactions that lead to the formation of the SEI.[12] Further research should focus on the electrode/electrolyte interface and SEI formation in PDC electrodes.

Operational safety is another concern for most metal-ion batteries. The formation of dendrites due to the accumulation of metal ions poses a serious safety threat, and an increase in dendrite size can lead to a short-circuiting and potential explosion. Electrode materials must be run within allowable voltage ranges to avoid these issues and increase cell life. Electrolytes used in the metal-ion batteries are usually a combination of flammable, organic compounds, that are susceptible to explosion.[13] Along with these problems, SIBs face a distinct set of challenges associated with the large size of the $Na^+$ ions. The selection of electrode materials is controlled by the size of the ions.[14] The incorporation of large $Na^+$ ions during intercalation/alloying leads to significant volume changes that results in structural degradation and pulverization. Si was also reported to be inactive as the anode in SIBs. However, PDC-derived carbon offers a defective and disordered structure with an oxygen-doped surface and expanded interlayer structure, thus enabling enhanced active sites for sodium storage. Drawbacks of PDC systems, such as voltage hysteresis and capacity degradation have been mitigated to some extent by introducing carbon nanomaterials such as graphene and carbon nanotubes in the PDC matrix.[15] The Si-O-C system is categorized by the appearance of stable Si-C and Si-O bonds, free carbon, and an overall amorphous structure. The formation of additional SiC domains at higher temperatures initiates capacity degradation.[16] The impact of pyrolysis atmosphere on SiOC composition, such as mixing hydrogen with argon, has been shown to cause significant evolution in carbon

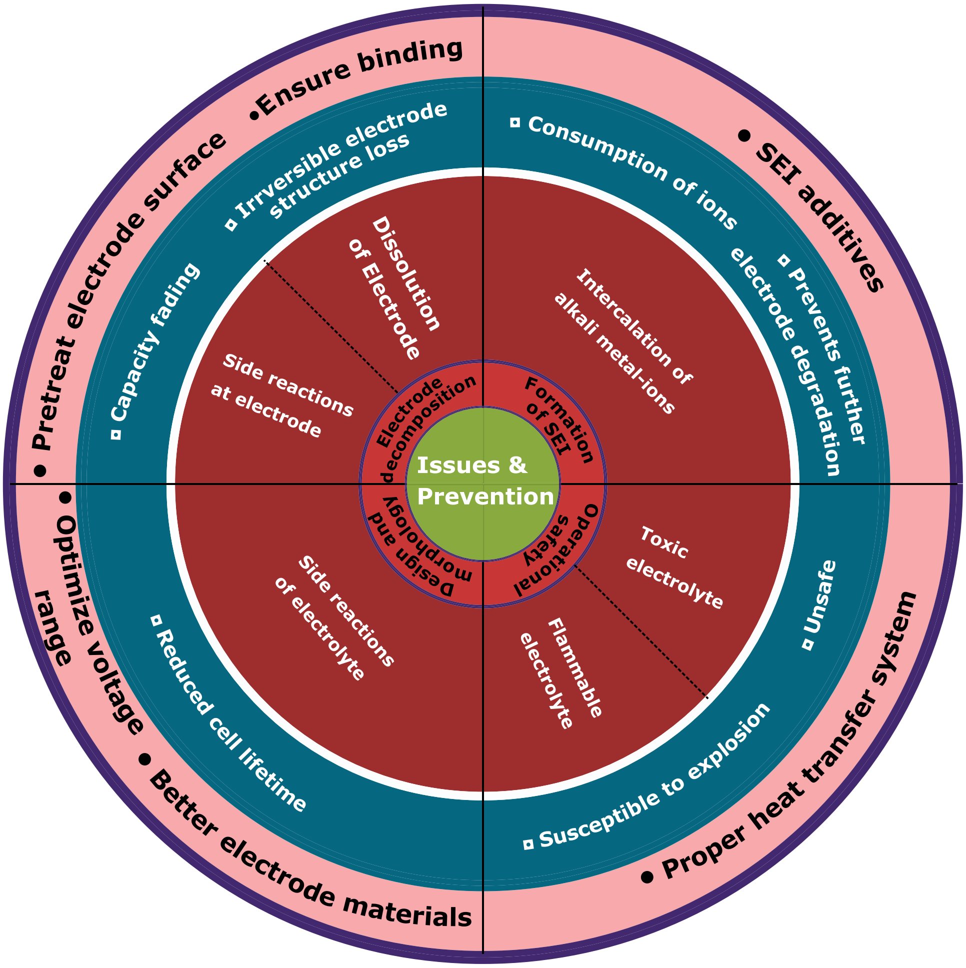

FIGURE 3 A chart representing the issues faced in electrochemical energy storage systems, their causes, effects, and prevention techniques to overcome the corresponding issues. Reproduced with permission.[4] Copyright 2012 Nanomaterials and Energy

concentration. Thermodynamic limitations and kinetics of Li-ion diffusion between various electrochemical potentials of Li-ions at SiOC-electrolyte-lithium interfaces have demonstrated hysteresis at a polarization potential of 250–500 mV.[17] However, having a different valency in the SiCN system, Si–N tetrahedra have been shown to influence electron density localization and diminish alkali-ion binding compared to a Si–O nanostructure. Therefore, future research on the PDCs as electrochemical energy storage should focus on the study of voltage hysteresis and the cycling effect on the internal resistance, as well as quantitatively compare various operating conditions.

Supercapacitors and batteries have similar complications. Fundamentally, electrode and electrolyte compatibility are essential for safe operation and stable performance of the supercapacitor. Low electrode mass and voltage range of ~1.2 V in an aqueous electrolyte significantly limit the overall energy density of the supercapacitor device. Maintaining stable cell performance throughout a large number of cycles (usually ≥20 000 cycles) without capacitance fading while keeping the cost of cell fabrication low are challenges that remain to be overcome.

A schematic representation of issues and preventions of electrochemical devices is presented in Figure 3.

## 5 | CONCLUSION

Adaptive fabrication techniques and unique properties make PDCs promising materials for many energy storage devices. The favorable electrochemical properties of PDCs are a direct result of their unique molecular or nanodomain structure which may only be obtained via the polymer pyrolysis route. Achieving desired phase composition and distribution in the amorphous matrix in PDCs requires effective utilization of the molecular precursor and processing conditions. The main benefits of PDCs over traditional graphite or hard carbon-based electrodes include superior energy density, rate capability, and long-term cycling stability. Nonetheless, there are issues that need to be overcome for the widespread use of PDCs in both metal-ion batteries and supercapacitors. These include relatively high energy-cost associated with processing and voltage hysteresis. Such concerns are lessened by achieving and maintaining higher capacities at higher cycling in PDCs than traditional graphite electrodes. In addition, recent works have shown that reducing the particle size of active PDC material, presence of free carbon phase, accommodating nanoporous thin film instead of bulk ceramic, or employing a PDC/C nanocomposite may further promote suitable ionic diffusion and thus provide sustainable storage capacity. Given the wide range of compositions possible in PDCs and sensitivity to pyrolysis conditions, future work may focus on the development of in-depth structure-property-processing correlations in a variety of PDCs toward $Li^+$ and $Na^+$ chemistries. In addition, there is a need for improved in-situ microscopy and spectroscopy characterization of the electrode/electrolyte interface in PDC electrodes.

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