JPhys Materials

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To cite this article: Murilo M Amaral *et al* 2023 *J. Phys. Mater.* **6** 021001

IOP Publishing *J. Phys. Mater.* **6** (2023) 021001 https://doi.org/10.1088/2515-7639/acbdef

Journal of Physics: Materials

ACCEPTED FOR PUBLICATION
15 February 2023

PUBLISHED
3 March 2023

PERSPECTIVE

A perspective on silicon-based polymer-derived ceramics materials for beyond lithium-ion batteries

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Keywords: silicon-based ceramics, polymer-derived ceramics, energy storage devices

Abstract

Energy storage devices beyond lithium-ion batteries (LIBs), such as sodium-ion, potassium-ion, lithium-sulfur batteries, and supercapacitors are being considered as alternative systems to meet the fast-growing demand for grid-scale storage and large electric vehicles. This perspective highlights the opportunities that Si-based polymer-derived ceramics (PDCs) present for energy storage devices beyond LIBs, the complexities that exist in determining the structure-performance relationships, and the need for *in situ* and operando characterizations, which can be employed to overcome the complexities, allowing successful integration of PDC-based electrodes in systems beyond LIBs.

1. Introduction

Lithium-ion batteries (LIBs) have been the most successful secondary battery technology after their commercialization in 1991, which was celebrated in the 2019 Nobel Prize of Chemistry awarded to Prof. Goodenough, Prof. Whittingham, and Dr Yoshino for their trailblazing contributions toward the development of LIBs [1]. Continuous improvement has been achieved in LIB technology through tremendous efforts, collaboration, and research in the past two decades. However, with the increasing demand for clean and renewable energy sources, LIBs are reaching their threshold energy density (~265 Wh Kg^{-1}), and the need for an alternate economic energy storage system with high energy density is apparent [2].

Since their introduction in the 1960s, silicon (Si)-based polymer-derived ceramics (PDCs) have shown novel chemical and physical properties. PDCs' exceptional synthesis route from the polymer-to-ceramic stage enables large variations in PDC properties by tuning their precursor structures and processing parameters. High electrical conductivity, chemical stability against electrochemical corrosion, and the advantage of cycling alkali-ions at room temperature have allowed PDCs to be utilized as high-energy density anodes in LIBs [3]. In addition, the desired pore size, volumetric porosity, and morphology are achievable from PDCs, which makes them a feasible choice for energy storage devices. Silicon (Si) is a prosperous choice for LIBs anodes because of its high theoretical capacity of ~3600 mAh g^{-1} and abundance [4]. Si-based PDCs can accommodate lithium ions in a potential range from 0 to 3 V, providing electrochemical capacities as far as 900 mAh g^{-1} and columbic efficiency higher than 99% [3].

However, there are some issues with LIBs, such as the use of cobalt on their positive electrodes for most of them, which has a limited supply chain, whose most resources are settled in precarious areas, which can negatively affect the cost of LIBs [5]. Limited resources of raw materials and the need for stationary storage systems call for improved technologies, aiming to satisfy the diversified application requirements. The next-generation alternative battery systems, such as sodium-ion batteries (SIBs), potassium-ion batteries (PIBs), and lithium-sulfur batteries (LSBs) have the advantage of implementing abundant materials, such as sodium, potassium, and sulfur [6, 7]. Supercapacitors can also play a crucial role in future sustainable

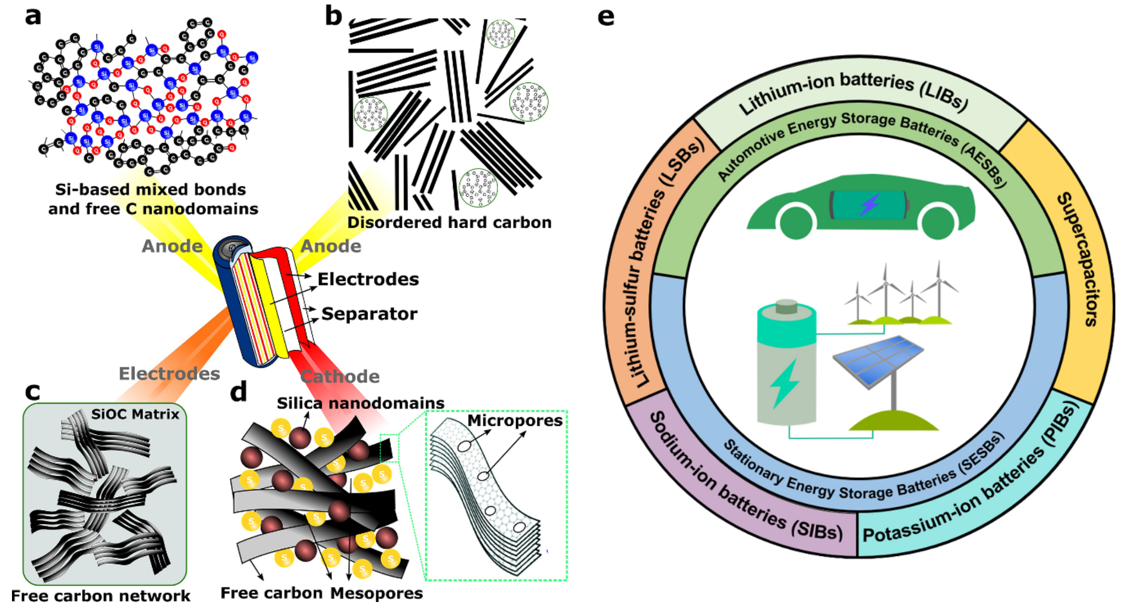

Figure 1. Schematics of charge storage structures of PDCs in rechargeable batteries and supercapacitors. Polymer-derived silicon oxycarbide (SiOC) is used as an example. (a) The atomic model of the SiOC ceramic consists of a free carbon phase, SiO_xC_y units, and nano-voids to store Li-ions. The ions are likely stored reversibly in the free carbon phase and irreversibly captured in the Si-O-C matrix. (b) The highly disordered carbon phase of the SiOC material is necessary for Na-ion batteries (SIBs). Na-ions are stored in the close vicinity to carbon layers and adsorbed on micropores. (c) In a supercapacitor, ions are adsorbed at the electrode surface of the free carbon network with high SSA derived from PDCs. (d) PDCs have been investigated as the sulfur host material in positive electrodes of LSBs batteries due to their conductivity, lightweight, and mechanical robustness. (e) Promising applications of various battery and supercapacitor technologies. Reprinted from [10], Copyright (2020), with permission from Elsevier.

electrochemical energy storage systems, which require electrodes with high specific surface area (SSA). Supercapacitors present high power density and long cyclability, but show energy density values lower than batteries [8]. The possibility of a wide range of compositions and flexibility in the tuning of PDC microstructure have allowed using PDC materials as the electrode of the corresponding LIBs, SIBs, supercapacitors, and LSBs technologies, as displayed in figures 1(a)–(d), respectively. The application of PDCs with alterable properties has demonstrated substantial capacity and cycle life beyond LIB electrode materials [3, 9]. Figure 1(e) details the application scenario of novel energy storage systems. The aim of this perspective is to present a general overview, and the recent advances in the application of Si-based PDCs in energy storage devices beyond the LIBs as studies involving LIBs have already been covered elsewhere [4, 9]. Moreover, a recent Review article by Wen *et al* [4] evidenced that PDC-based electrodes have been rarely investigated for energy storage devices beyond LIBs further justifying the need for a forward-looking perspective on this topic.

2. Application of silicon-based PDCs as electrodes of energy storage devices beyond Li-ion technology

2.1. Silicon-based ceramics as negative electrodes of SIBs

SIBs are considered a complementary alternative to LIBs owing to abundant sodium resources, thus presenting a low cost [5]. However, it is necessary to investigate novel materials for the negative electrode of SIBs, which should properly cycle sodium ions and present a high reversible capacity. Hard carbon (HC) is considered a good anode for SIBs due to its suitable microcrystalline framework for Na^+ ion intercalation and gravimetric capacity higher than 300 mAh g^{-1} [11]. Si-based PDCs or HC derived from PDCs can be an alternative to the negative electrodes of SIBs, as well as composites of HC and PDCs. Kaspar *et al* [12] employed a novel SiOC(N)/HC composite as the negative electrode of an SIB, which has shown higher capacity than pure HC. Also, Si-based ceramics functionalized with nanofillers can be applied as the anode of SIBs, such as the study conducted by Lim *et al* [13], which investigated nitrogen-doped polyfurfural-derived carbon/MoS_2 coated with SiOC (N-MoS_2/C@SiOC) as the anode for SIBs. This Si-based ceramic material provided reversible storage of sodium ions, reaching a capacity of 540.7 mAh g^{-1}, showing excellent capacity retention after 500 cycles, as shown in figure 2, which presents the reversible capacity of PDC-based materials for SIBs. Several studies investigated SiOC and SiOC composites in this regard. SiOC composites (e.g. with

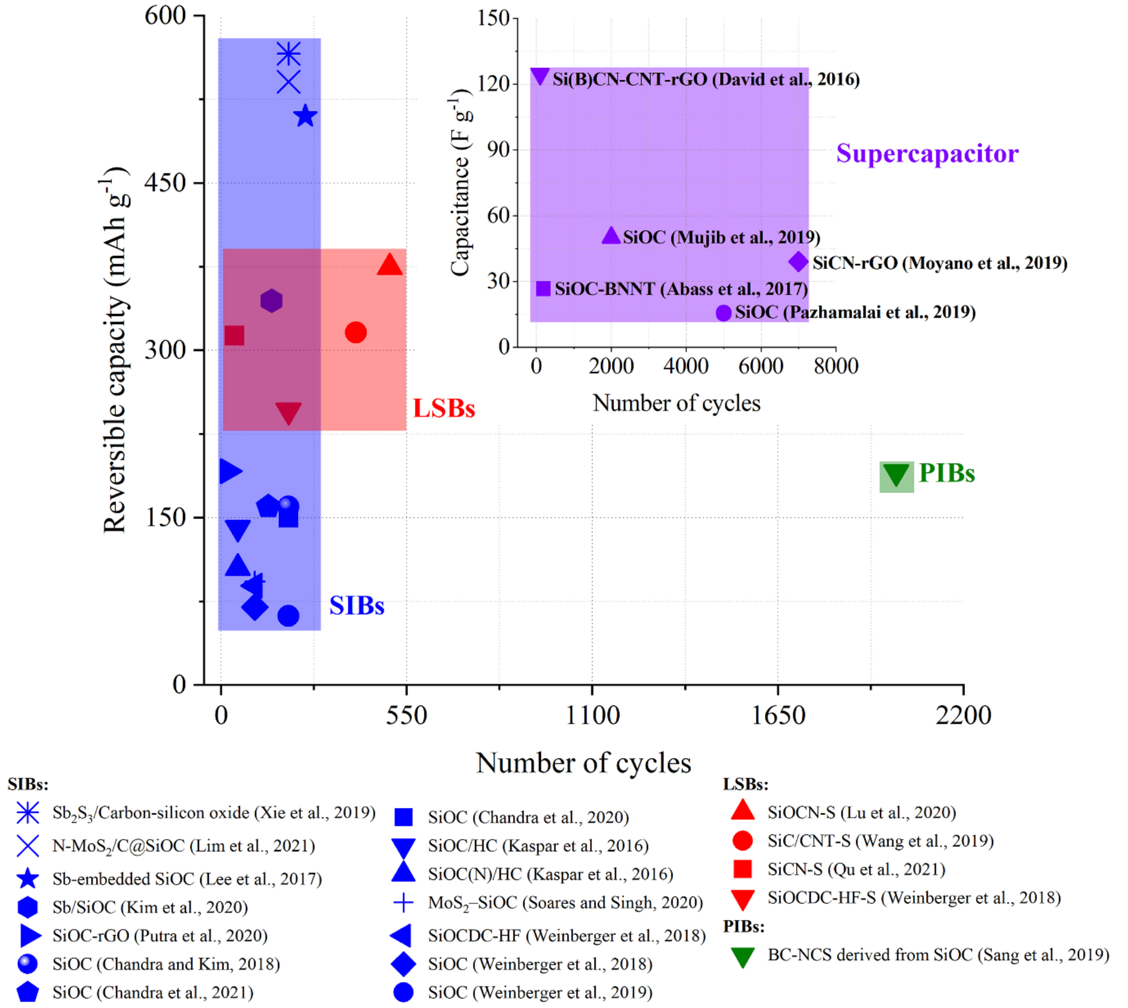

Figure 2. High-capacity PDC materials, and their respective reversible capacities at determined number of cycles, reported in the literature as the anodes of SIBs [12–19, 23–26], as the cathodes of LSBs [19, 27–29], and as the precursor for anodes of PIBs [22]. Inset: Capacitance retained after cycling tests of supercapacitors using PDC materials as their electrodes [30–34].

Sb, Sn, etc) have shown higher reversible capacity [14–16] than that of SiOC [17–19], in which SiOC works as a buffer material to volume expansion of alloy materials and prevents capacity fading. In addition, Weinberg *et al* reported carbide-derived carbon (CDC) obtained from PDC as the anode of SIBs [19]. In this work, the application of CDC derived from SiOC in SIBs reached the capacity of 89 mAh g^{-1} after 100 cycles. The performance of CDC in SIBs showed a minor increase compared to SiOC, suggesting that for SiOC the capacity was not entirely derived from free carbon phase.

2.2. Silicon-based ceramics as the precursor for negative electrodes of PIBs

PIBs present high energy density, low cost, and the advantage of having abundant potassium resources. However, PIBs have some restrictions regarding their practical application, such as low ion diffusion and volume expansion during the insertion processes of potassium ions [20].

A recent study conducted by Chandra *et al* [21] involving SiOC electrodes showed that electrochemical insertion-extraction of alkali metal-ions such as Li$^+$, Na$^+$, and K$^+$ in SiOC follow the same general mechanism. The ions are stored in the microvoids of SiOC structure initially. A further insertion of ions creates Si–C and Si–O bond cleavage resulting in the formation of large-size free volume, which facilitates additional sites for ion insertion. However, the material presented a low capacity to the potassium ion system since a lower number of ions were inserted due to a repulsive interaction between them. The SiOC material also showed a huge volume expansion during potassiation, which indicates that the application of this material as the anode of PIBs is more challenging than its applications in SIBs.

Also, PDCs can be used as the precursors for porous carbon materials, which can accommodate large-sized potassium ions. In a study conducted by Sang *et al* [22], carbon-rich SiOC was used as the precursor for bi-continuous nanoporous carbon spheres, which was employed as the anode for PIBs, showing considerable capacity retention for potassium storage with a reversible capacity of 191 mA g^{-1} after

2000 cycles. This study showed a novel alternative for using ceramics as the precursor of anode materials for PIBs. Figure 2 summarizes Si-based PDCs applied as the electrodes of LIBs, SIBs, and LSBs, reported in the literature, with promising results of reversible capacity during a long number of cycles.

2.3. Silicon-based ceramics as electrodes of supercapacitors

Supercapacitors are energy storage devices that present high power density and high cyclability. The electrodes used in supercapacitors should present certain characteristics such as high SSA, conductivity, and resistance to corrosion [8]. Therefore, Si-based PDCs, such as silicon carbonitride (SiCN) and SiOC, can be considered an option for supercapacitors electrodes [35]. Chemical interfacing of PDCs with carbon materials can also be used as the electrode of supercapacitors. For example, David *et al* [30] studied boron-doped SiCN composited with carbon nanotube (CNT) and reduced graphene oxide (rGO) as the electrode for aqueous supercapacitors. The Si(B)CN-CNT-rGO electrode showed the highest capacitance value of $\sim$269.52 F g^{-1}, resulting from the reduced internal resistance of the electrode due to the formation of an interconnected conductive network. In PDC-based supercapacitor electrodes, the charge is stored at or near the surface of the electrodes. Thus, PDCs with high SSA and electronic conductivity hold great potential as electrodes of electrochemical double-layer capacitors. Si-based PDCs have already been used as electrodes for supercapacitors, as the study conducted by Mujib *et al* [36], which investigated the application of freestanding carbon-rich SiOC as an electrode for aqueous supercapacitors. These electrodes were fabricated from siloxane oligomer precursors, and showed excellent capacitance retention of almost 100% of its initial capacitance after 5000 cycles. These results indicate that PDCs present considerable advantages for use in supercapacitors. The cyclability results of several supercapacitors, comprising PDCs as their electrodes, can be observed in the inset of figure 2, which presents the retained capacitance as a function of cycle number.

2.4. Silicon-based ceramics as a sulfur host for positive electrodes of lithium-sulfur batteries

LSBs use sulfur as the positive electrode's active material, presenting excellent advantages, such as an exceptional theoretical capacity of 1675 mAh g^{-1} and an impressive energy density of $\sim$2600 Wh Kg^{-1}. However, these systems have drawbacks, such as low conductivity, high-volume expansion of sulfur ($\sim$80%), and the formation of intermediate lithium polysulfides. The latter briefly consists of the electrochemical conversion of sulfur to Li_2S, which is diffused into the lithium metal negative electrode, according to the *shuttle effect*. This process culminates in an irreversible loss of sulfur from the positive electrode, decreasing the battery's energy density, and resulting in a significant decrease in the cyclability of LSBs systems [37].

PDC materials, such as SiCN and silicon oxycarbonitride (SiOCN), have demonstrated the ability of chemically and physically adsorb lithium polysulfides as the cathodes in LSBs [29]. The SiOCN ceramics investigated by Lu *et al* [29] presented meso/macropores, and their ability to adsorb lithium polysulfides was proved by x-ray photoelectron spectroscopy (XPS) analysis. Composite PDC-carbon electrodes are another alternative for the cathodes of LSBs, as indicated in the study by Wang *et al* [27], which reported the application of a composite material containing CNTs and silicon carbide (SiC) as the sulfur host. The chemical adsorption of lithium polysulfides by the electrodes was proved by density functional theory (DFT) calculations, and S-CNT/SiC showed higher efficiency than the S-SiC electrode in the adsorption of polysulfides. Thus, the use of PDCs as the cathodes of LSBs has demonstrated efficiency in hosting sulfur into their structure, and trapping intermediate polysulfides. Figure 2 presents the reversible capacity of PDC materials applied as the cathodes of LSBs.

Further research on the application of PDCs as the host material of LSBs' cathodes can enable the design of systems with higher electrochemical stability, and long cycling life, by overcoming the shuttle effect. CDC obtained from PDCs can also be applied in LSBs as reported by Weinberger *et al* [19], which showed the application of carbon spheres derived from SiOC in the cathode of an LSB system. This material showed an excellent rate capability providing a reversible specific capacity of 241 mAh g^{-1} at 500 mA g^{-1} after 100 cycles, whereas a nearly similar value of 246 mAh g^{-1} was achieved when cycled at 100 mA g^{-1}.

3. Recent advances and challenges for PDCs in modern energy storage devices

The usage of PDCs as electrodes provide outstanding capacity and cycling life for energy storage devices, as detailed in figure 2. However, further studies need to be carried out to overcome some remaining issues, such as the high-capacity loss of the initial cycle and voltage hysteresis (or the energy inefficiency of the cell) at the PDC-electrolyte interface due to thermodynamic limitations and the kinetics of metal-ion diffusion as shown in figure 3 [3, 38].

Thus, further research and progress on these materials would undoubtedly contribute to developing novel lightweight and flexible energy storage devices with high capacity and long cyclability. To have progress in the research of PDCs battery electrodes, and overcome the shortcomings mentioned above, there are two

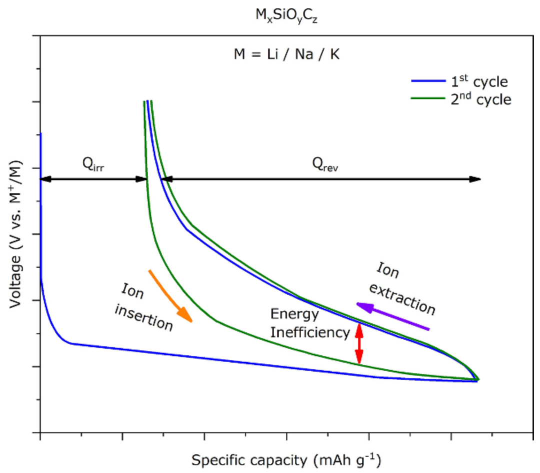

Figure 3. The energy inefficiency of polymer-derived SiOC in metal-ion batteries. Adapted from [39], Copyright (2010), with permission from Elsevier.

prevailing concern areas: (a) lack of understanding of the structure of PDCs, such as the porosity (e.g. shapes, sizes, etc), elemental composition, and amorphous phases, and (b) challenges in monitoring structural and elemental changes on PDC electrodes directly.

There is a lack of understanding of the complex architecture of PDCs as they present amorphous and crystalline phases, small sizes, and diverse and disordered atomic structures [40, 41]. Also, PDC materials present structural and porous changes during pyrolysis processes, which are influenced by the temperature, precursor, and atmosphere [3, 41, 42]. These structural changes from polymer precursor to ceramic can be investigated by several spectroscopy techniques, such as XPS [43], Fourier-transform infrared (FTIR) [44], Raman [45], and nuclear magnetic resonance (NMR) [46] spectroscopies. However, different phenomena require the use of particular techniques. For example, the decomposition mechanism of the precursor and the existence of functional groups can be investigated through FTIR spectroscopy [44]. PDC materials, such as SiOC, have shown free carbon in their structure [45], which can be predicted by Raman spectroscopy. Likewise, the free carbon cluster size in ceramics can also be investigated by Raman spectroscopy [47]. The effects of the annealing process (such as temperature and time) on the formation of amorphous and crystalline phases in PDCs can be studied by small angle neutron scattering (SANS), but this technique is not capable of penetrating the bulk of the samples [48]. Also, the bonding environments, carbon segregation, and the formation of amorphous species during the annealing process, such as Si_3N_4-nanodomains in SiCN and SiO_2 domains in PDC materials, can be investigated by NMR spectroscopy [46]. Smaller SiC crystal phases (2–10 nm) in the selected area of Si-based PDCs can be detected by the use of high-resolution transmission electron microscopy (TEM). The elemental phases and drawbacks from conversion processes can be identified through XPS by monitoring the chemical composition of the precursor and the PDC [43]. The contribution of these characterization techniques is detailed in figure 4(a). On the other hand, it is essential to investigate PDC electrode materials under dynamic conditions, to directly monitor their structural and elemental changes by *in situ* and operando analyses, which consist of coupling characterization techniques (e.g. spectroscopy and microscopy) with electrochemical tests (e.g. galvanostatic charge–discharge). These procedures require the use of specific apparatus, such as spectro-electrochemical cells for *in situ* spectroscopy techniques [49, 50], and electrochemical cells designed for scanning electron microscopy (SEM) [51] and TEM [52] .

As far as we know, the behavior of PDC materials as electrodes for energy storage devices has not yet been investigated by *in situ* characterization techniques. However, based on the knowledge available, several *in situ* techniques can be employed to investigate the PDCs electrodes. For example, the formation of the solid-electrolyte interphase (SEI) layer on the anodes (e.g. PDC material) of metal-ion batteries can be monitored by *in situ* Raman and FTIR spectroscopies [53]. Beyond metal-ion batteries, other phenomena, such as the formation of lithium-polysulfides (LPs) in LSBs, can be monitored by *in situ* FTIR, Raman, ultraviolet-visible, and x-ray absorption (XAS) spectroscopies [54]. Also, the intercalation processes on electrodes can be monitored by NMR spectroscopy, which can support the design of novel electrode materials [55]. Beyond spectroscopy techniques, PDCs electrode morphological changes, such as the formation of dendrites on lithium-metal electrodes, can be identified by *in situ* SEM [56] and TEM [57]. The contributions of *in situ* techniques for overall energy storage devices are summarized in figure 4(b).

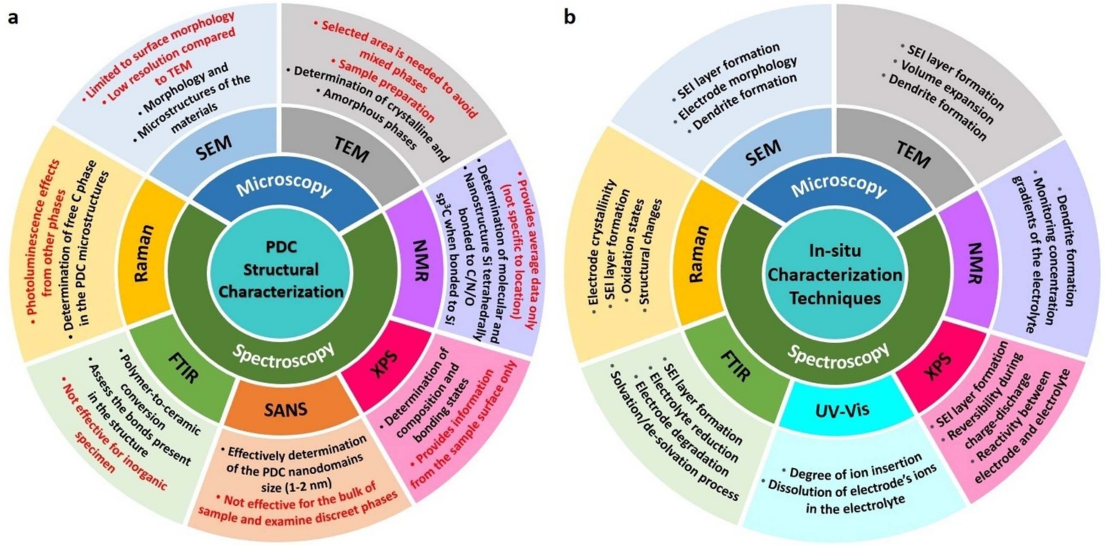

Figure 4. (a) Contributions of ex situ microscopy and spectroscopy techniques to PDCs materials. (b) Contributions of *in situ* and operando microscopy and spectroscopy techniques for energy storage devices.

4. Conclusion

Silicon-based ceramics, particularly PDCs and their composites, have presented various opportunities as high-capacity electrodes for energy storage devices. These materials are low-density open amorphous structures and present mechanical robustness, which are significant characteristics of an electrode material. PDCs have been applied as the electrodes of supercapacitors, anodes of metal-ion batteries (e.g. LIBs and SIBs), and sulfur hosts for the cathodes of LSBs. Silicon-based ceramics have demonstrated efficiency in adsorbing lithium polysulfides and inhibiting the shuttle effect, a major drawback that restricts the practical applications of LSBs. However, the materials mentioned in this perspective have rarely been investigated for batteries beyond Li-ion technology. Proper utilization of the precursors and processing conditions are necessary to achieve the desired structure and phase composition of the PDCs. The structural characterization of the PDCs during the precursor-to-ceramic transformation process will help to determine the composition, crystallization, and decomposition behavior. The potential applications of PDCs beyond LIBs can be adequately evaluated based on their composition and functional properties. *In situ* and operando characterization techniques are needed to understand structural and elemental changes under polarization conditions, such as the formation and evolution of SEI at the PDCs/electrolyte-ion interface, stability/degradation of the PDC electrodes, intercalation of metal ions, and formation of lithium polysulfides in LSBs. The progress on these materials, which are promising choices for large-scale applications, will permit the development of novel advanced energy storage devices with high capacity and long cycling life.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: www.NNN.org/download/.

Acknowledgments

G Singh and S B Mujib would like to acknowledge Kansas State University for providing financial support. They also are grateful for the National Science Foundation Grant (Award Number: 1743701) and CMMI NSF CAREER Grant (Award Number 1454151). M M Amaral would like to acknowledge Kansas State University and the UNICAMP Development Foundation for providing financial support. M M Amaral and H Zanin would like to acknowledge the financial support from the Brazilian funding agencies CNPq (310544/2019-0-PQ-2 Grant), FAPESP (2017/11958-1, 2014/02163-7), and the support from Shell and the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas, and Biofuels Agency) through the R&D levy regulation.

Conflict of interest

The authors declare that they have NO affiliations with or involvement in any organization or entity with any financial interest in the subject matter or materials discussed in this manuscript.

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