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Porous reduced ceramic monoliths derived from silicon- and titanium-based preceramic polymer gels

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Preceramic polymer routes, which produce ceramic products called polymer-derived ceramics (PDCs) from molecular precursors, have been developed as a powerful tool to synthesize reduced ceramics in different morphologies (fibers, coatings and monoliths) for over half a century. In recent years, pore control of porous ceramic monoliths has attracted attention for improving their functionalities, which has driven the preceramic polymer routes to be integrated with other synthetic techniques for porous materials such as templating, foaming, emulsion and phase separation. This article briefly overviews porous PDC monoliths with a special emphasis on those derived from porous preceramic polymer gels which are prepared via the sol–gel process accompanied by spinodal decomposition. Ceramization behaviors of Si- and Ti-based preceramic polymers are highlighted in terms of crystal transition and variation of pore properties in different length scales.

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1. Introduction

Porous ceramic materials are characterized by low density and high specific surface area in addition to various physical properties derived from each ceramic constituent, and therefore utilized in multifold fields such as catalysis, separation, energy storage, and so forth. In particular, reduced ceramics represented by non-oxides like carbides and nitrides often show unique physicochemical features in term of optical, magnetic, electrical and electrochemical properties that are not observed in common oxides.^{1)–6)} Nevertheless, the number of studies on porous reduced ceramics is fairly small compared to the oxide counterparts. This is probably due to the difficulty in synthesis of reduced ceramics and control of their porosity. For example, one of the most developed means to fabricate porous ceramics is the sol–gel process: a myriad of porous ceramics have been produced by a variety of synthetic strategies based on sol–gel chemistry.^{7)–10)} However, materials directly prepared by the sol–gel technique are mostly oxidized phases, and an additional reduction process is mandatory, which requires considerably high temperature and a controlled atmosphere together with a long processing time. This heat-treatment process in harsh condition often causes undesirable crystal growth, thereby making it

difficult to preserve original porous structure of sol–gel products.

Meanwhile, the so-called preceramic polymer route has come forth as a methodology for obtaining reduced ceramics from the aspect of molecular chemistry, where inorganic–organic hybrid polymers are converted to non-oxide ceramic materials.^{11)–13)} Thus prepared materials are known as polymer-derived ceramics (PDCs). This technique allows for efficient and homogeneous ceramization and crystallization since the elements of objective ceramic products are mixed at the atomic level in the precursor polymer, and one can decrease the calcination temperature and duration time. The PDCs have been actively studied for a long time mainly on Si-based ceramics since the pioneering research on the synthesis of silicon carbide (SiC) fibers using polycarbosilane as a precursor.¹⁴⁾ Nowadays, we can find diversified PDCs like Al-, Ti- and Zr-based ceramics in the literature.^{15)–17)} The PDCs have been developed with respect to the material morphology as well. In the early days, researchers focused on fibrous materials and ceramic coating. Afterward, in the last few decades, the main target shifted to porous PDCs in a monolithic form. The synthetic approaches to tailor porous structure in a PDC monolith reported to date include the templating, foaming, emulsion and phase separation.¹⁸⁾

This article outlines the porous PDC monoliths and their derivatives prepared from the preceramic polymer gels whose porous structure is tailored by the phase separation

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Fig. 1. Schematic illustration showing the synthesis of porous PDC monoliths by combining the preceramic polymer route and the phase separation method.

method (Fig. 1). In this strategy, the co-continuous macroporous geometry with controlled pore properties (size and volume) is formed in a precursor gel by inducing the spinodal decomposition in a series of sol-gel systems.^{10),19),20)} Calcination of the precursor gels under inert atmosphere gives rise to the porous PDC monoliths preserving the original macropores. Here, the Si- and Ti-based systems are overviewed with an emphasis on the author's works. In the Si-based system, the porous SiC and silicon oxycarbide (SiOC) ceramics derived from the bridged polysilsesquioxanes are demonstrated in terms of the relationship between the type of polysilsesquioxane and the ceramization behavior. The porous carbon monoliths with high surface area derived from the SiOC monoliths are briefly presented as well. In the Ti-based system, a concise picture on various reduced ceramics prepared from the Ti-ethylenediamine (EDA) hybrid gels are presented.

2. Porous Si-PDC monoliths

2.1 Porous bridged polysilsesquioxane monoliths

Bridged polysilsesquioxane gels are obtained by the hydrolysis and polycondensation reaction of the corresponding organoalkoxysilanes in which the organic group is directly bonded to two neighboring silicon atoms. The chemical formula of the condensates is ideally $RSiO_{3/2}$, and thereby called as polysilsesquioxane. By contrast to the trialkoxysilanes equipped with dangling organic groups, which hardly result in homogeneous gelation due to the steric hindrance, the bridge-type organoalkoxysilanes readily forms a gel by the sol-gel reaction, though both types of alkoxysilanes yield polysilsesquioxanes.^{20),21)} In view of the better controllability of the sol-gel reaction, the porous Si-containing preceramic polymer gels were fabricated from three different bridged alkoxysilanes: 1,2-bis(trimethoxysilyl)ethane (BTME), 1,4-bis(triethoxysilyl)benzene (BTEB) and 4,4'-bis(triethoxysilyl)biphenyl (BTEBP) [Fig. 2(a)].

The polymer network derived from BTME shows hydrophilic nature owing to the compact ethylene group.

Fig. 2. (a) Chemical structures of the bridged alkoxysilane precursors and (b) representative macroporous structures of the corresponding porous bridged polysilsesquioxane gels prepared by the phase separation method.

Hence, the porous gels with co-continuous macroporosity can be prepared by the synthetic protocol similar to the well-established system of the porous silica gels, where spinodal decomposition is induced by adding poly(ethylene oxide) in an acid-catalyzed sol-gel process.^{22),23)} On the other hand, since the polymer networks having the bulky arylene groups become hydrophobic, the BTEB- and BTEBP-derived sol-gel reactions in aqueous media result in precipitates unless employing a specific elaborate technique.^{24)–27)} It was found that homogeneous gelation is allowed in a polar organic solvent such as amides by improving the compatibility between the hydrophobic gel phase and the solvent phase. By adding a phase separation inducer to these sol-gel systems, one can tailor co-continuous macropores in both phenylene- and biphenylene-bridged polysilsesquioxane gels.^{28),29)} As such, three types of bridged polysilsesquioxane gels with analogous macroporous morphologies were prepared as displayed in Fig. 2(b).

2.2 Ceramization into porous Si-PDC monoliths

Considering the thermal decomposition of different bridged polysilsesquioxanes in an inert atmosphere, it is expected that the preceramic polymer with higher C/Si ratio yields more reduced ceramics leaving a larger amount of carbon. The thermogravimetric analysis (TG-DTA) results of the three bridged polysilsesquioxane networks under Ar atmosphere are compared in Fig. 3(a). Note that the additive polymer employed as the phase separation inducer was removed prior to the TG measurements. All the bridged polysilsesquioxanes showed the similar behaviors involving the three-step weight loss at <800, 800–1200 and >1200 °C. It is reasonable that the initial pyrolysis of organic moieties takes place spinning off carbonaceous species below 800 °C, which was testified by the FT-IR measurements.^{28),29)} From 800 to 1200 °C, further carbonization of carbonaceous components occurs. The X-ray diffraction (XRD) profiles of the samples calcined at different temperatures shown in Fig. 3(b) indicate that the PDCs remained amorphous, i.e. SiOC, at 1200 °C and that the crystallization to SiC required >1200 °C. The relatively small and gradual weight loss above 1200 °C is

therefore attributable to the carbothermal reduction toward β -SiC, which consumes the carbon species. It is found from the XRD results that the samples calcined at 1500 °C contained cristobalite (SiO_2) starting from the ethylene-bridged (BTME; C/Si = 1) and phenylene-bridged (BTEB; C/Si = 3) polysilsesquioxanes, whereas no XRD peaks other than SiC are observed in the biphenylene-bridged counterpart (BTEBP; C/Si = 6).

The degree of reduction for each PDC sample, in other words, the amounts of SiC and residual carbon can be estimated by investigating the thermolysis of the calcined

Fig. 3. (a) TG–DTA curves under Ar atmosphere of the porous bridged polysilsesquioxane gels derived from different alkoxy-silanes. (b) XRD patterns for the porous Si-PDC monoliths obtained by calcining different preceramic polymer gels at varied temperatures under Ar atmosphere.

samples in air [Fig. 4(a)]. The weight loss at 400–700 °C is attributed to the pyrolysis of amorphous carbon, while the weight increase at >700 °C is associated with the oxidation of SiC crystals. The higher onset temperature for the oxidation indicates the larger SiC crystals grown in the PDCs. The estimated carbon contents and the weight increase of Si-ceramics excluding the carbon during oxidation in each sample are summarized in Fig. 4(b). When SiC is fully oxidized to SiO_2 , the weight increases by 50 %, which is signified by the broken line. It indicates that the carbon content in the phenylene-bridged polysilsesquioxane fell short of the thorough reduction to produce pure SiC ceramics resulting in the SiC/SiOC composites, let alone ethylene-bridged one. On the other hand, the biphenylene-bridged polysilsesquioxane yielded the SiC/C composites by the calcination at >1300 °C. As the combustion temperature of carbon is much lower than that for the oxidation of SiC as shown in Fig. 4(a), the SiC ceramics without carbon can be obtained by firing the BTEBP-derived PDCs in air.²⁹⁾ The TG results also testify that thus obtained SiC ceramics show high thermal resistance being stable in air without oxidation up to approximately 800–900 °C.

Figure 5 shows the variation of macroporous morphologies for a set of Si-PDC monoliths. It is confirmed that the macroporous structure was well-preserved in the discrete PDCs. It is worthwhile noting that the PDC monoliths derived from the phenylene-bridged precursors possessed the smaller pores as interstices of crystallites with relatively narrow pore size distribution in the macropore skeleton, resulting in the hierarchically porous PDC monoliths.²⁸⁾ The mean mesopore size increased as the calcination temperature was elevated because of the enhanced crystal growth. By contrast, in the case of the samples derived from the biphenylene-bridged ones, the mesopores originated from the precursor persisted after the calcination probably with the aid of amorphous carbons.²⁹⁾

Fig. 4. (a) TG curves in air for the porous Si-PDC monoliths obtained by calcining different preceramic polymer gels at varied temperatures. (b) Estimated carbon contents and weight increase ratios by the oxidation of reduced Si-based phase excluding carbon moieties in each Si-PDC monolith.

Fig. 5. Variation of macroporous morphologies on heating under Ar atmosphere for a series of porous PDC monoliths derived from different bridged polysilsesquioxane precursors.

2.3 Nano-phase extraction of porous SiOC monoliths towards porous carbon monoliths

As mentioned in the foregoing section, the calcination of bridged polysilsesquioxanes at $<1200\text{ }^{\circ}\text{C}$ yielded amorphous SiOC, which can be regarded as silica/carbon nanocomposites in which Si/O-based nano-domains are homogeneously distributed in amorphous carbon matrix³⁰⁾ while involving Si–C bonds.^{28),29)} It means that hierarchically porous carbon monoliths with enhanced specific surface area can be prepared by selectively removing the Si/O nano-domains;³¹⁾ the resultant carbon monolith is supposed to be enriched with micropores owing to the nano-phase extraction in addition to the macropores and mesopores originated from the precursor gel. In this context, the porous carbon monolith was prepared from the BTEBP-derived PDC calcined at $1200\text{ }^{\circ}\text{C}$ by etching in a NaOH solution. The pore characterization by microscopic observation and N_2 physisorption verifies that the amount of micropores and thus specific surface area effectively increased retaining the macro- and mesoporosity under the abovementioned scenario (Fig. 6).^{32)–34)}

In general, the production of porous carbons with a specific surface area of $>1000\text{ m}^2\text{ g}^{-1}$ requires the thermal activation process either physically or chemically.³⁵⁾ The porous carbons with high surface area synthesized through the thermal activation are denoted as “activated carbons”. One can produce activated carbons with different micropore size distributions by treating carbons under varied thermal conditions (temperature and atmosphere), which, however, also govern the surface functionalities. On the contrary, it was revealed the nano-phase extraction approach can change the micropore properties of porous carbons by varying the hydrothermal treatment for precursor polysilsesquioxane gels.^{33),34)} It indicates that this path-

Fig. 6. Fabrication of hierarchically porous carbon monolith with high surface area from the Si-PDC monolith via the nano-phase extraction approach.

way allows the micropore feature of the carbon monoliths to be modulated without dramatically changing the surface chemical property when the carbons experience the same thermal history. These carbon monoliths are useful in energy storage fields, for example, to probe the effect of micropore properties on the formation of electric double layers in various electrolytes.³⁴⁾

3. Porous Ti-PDC monoliths

3.1 Ti-based preceramic polymer gels toward porous Ti-PDC monoliths

Unlike the Si-based system described above, organotitanium compounds containing Ti–C bonding are extremely

Fig. 7. Schematic illustration presenting the Ti-based preceramic polymer system: control of macroporous morphologies for the Ti-EDA preceramic polymer gels and their crystal transition behaviors on calcination under Ar and N₂ atmospheres.

unstable and difficult to be applied to the sol-gel process for monolithic products.¹⁷⁾ Meanwhile, titanium alkoxides are also reactive and readily hydrolyzed in presence of H₂O, giving rise to TiO₂ precipitates. Hence, in order to elaborate Ti-based preceramic polymer gels, the non-hydrolytic sol-gel reaction³⁶⁾ needs to be employed. In view of efficient synthesis of reduced ceramics from a precursor containing less Ti–O bonds, the use of diamine such as hydrazine and EDA as a cross-linker appears to be favorable.³⁷⁾ Although commonly used titanium alkoxides also react very quickly with EDA, the addition of a chelating agent such as acetylacetone (AcAc) can suppress the reactivity of alkoxides and offer a better control of the sol-gel reaction. Accordingly, the porous Ti-EDA preceramic polymer gels with controlled pore sizes were successfully prepared by the non-hydrolytic sol-gel process accompanied by phase separation as displayed in **Fig. 7**.^{38),39)} Note that the Ti-EDA networks included AcAc as well even after drying.

Since anatase is a stable crystal phase and hence easy to form, the amorphous Ti-EDA gel networks initially transformed to the anatase/carbon nanocomposites, in which both anatase and carbon are doped with nitrogen, on heating.³⁸⁾ At elevated temperatures, the carbothermal reduction of titania proceeded giving rise to a series of reduced titanium oxide phases such as Magnéli phases (Ti_nO_{2n-1}). Simultaneously, the Ti-PDC was also subjected to nitridation by N-containing gases generated by the pyrolysis of N-doped carbon species. It is known that the nitridation of titania takes place by N₂ gas under carbothermal conditions.⁴⁰⁾ Therefore, the Ti-PDCs in this preceramic polymer system underwent the complicated ceramization and crystallization pathways, which is dependent on the calci-

nation atmosphere.³⁹⁾ When calcined under Ar atmosphere, the crystal phases of the Ti-PDCs transformed to Ti₄O₇ at 800 °C, γ-Ti₃O₅ at 1000 °C, a mixture of Ti₂O₃ and rock-salt titanium oxynitride (TiO_xN_y) at 1200 °C, and a single-phase of TiO_xN_y at 1400 °C. Under N₂ atmosphere, on the other hand, a mixture of Ti₄O₇ and TiO_xN_y was initially formed at 800–1000 °C followed by the thorough crystal transition to TiN at >1200 °C.^{38),39)}

Similar to the Si-PDC monoliths, the Ti-PDC ceramics obtained from the porous Ti-EDA preceramic polymer gels also maintained the original macroporous structure.^{38),39)} As for the skeletal pores (small pores embedded in the macropore skeleton), no distinct mesopores but micropores were evolved resulting in 140–200 m² g⁻¹ at <1000 °C. Meanwhile, the sample calcined at 1200 °C contained mesopores as interstices of hundreds nanometer-sized crystallites due to the expenditure of amorphous carbons that fill the interparticle spaces at lower temperatures.

The calcination of the porous Ti-EDA gels in air resulted in the N-enriched anatase and rutile monoliths with the co-continuous porosity,⁴¹⁾ which is outside the scope of preceramic polymer route though.

3.2 Electrochemical applications of porous Ti-PDC monoliths

Reduced Ti-based ceramics are electronically conductive owing to the 3d-electrons. In particular, some oxide phases such as Ti₄O₇ exhibit higher conductivity than amorphous carbon,⁴²⁾ and, furthermore, the series of rock-salt phases (TiO, TiN and TiC) show metallic behavior.^{43),44)} Hence, the porous Ti-PDC monoliths are attractive as electrode substrates owing to the good chemical stability, high specific surface area and excellent electronic conductivity. Indeed, the Ti-PDCs calcined at 1200 °C under Ar and N₂ atmospheres were imbued with the hierarchical porosity as well as the conductivity of >200 S cm⁻¹.^{38),39)} The porous TiN monoliths are also promising as a high-rate pseudocapacitor electrode.^{45),46)}

The Ti-PDCs heat-treated at lower temperatures have a potential in the application of Li-ion storage as presented in **Fig. 8**.³⁸⁾ The nanosized anatase crystals have an advantage of short diffusion of Li⁺ ions in solids. In addition, the N-doping to anatase distorts the Ti–O lattice enhancing the Li-ion accommodation and thereby increasing the electrode capacity.⁴¹⁾

4. Summary and future perspectives

This review demonstrates a part of the author's studies on porous reduced ceramic monoliths by the combinational synthetic strategy of the preceramic polymer route and the phase separation method. In the Si-based systems, the hierarchically porous PDC monoliths composed of carbon, SiOC, SiC and their composites can be prepared from a series of bridged polysilsesquioxane gels. In the Ti-based systems, the Ti-EDA precursor gels with controlled macropore size are producible by the non-hydrolytic sol-gel reaction accompanied by phase separation. The obtainable PDC monoliths from the Ti-EDA

Fig. 8. (a, b) Galvanostatic charge and discharge curves of the Ti-PDC electrodes at 20 mA g^{-1} in 1 M LiClO_4 (ethylene carbonate/diethyl carbonate): (a) 600°C in Ar and (b) 700°C in Ar. (c) Rate performances of the two electrodes.

preceramic polymer gels include N-doped reduced titanium oxide phases and rock-salt TiO_xN_y , which have high potential in the electrochemical application fields due to the porous geometry and high electronic conductivity.

On the background of increasing demand for functional materials, the importance of porous ceramics is still growing. Nonetheless, the variation of porous PDCs reported so far is still limited; only two systems (Si- and Ti-based PDCs) are demonstrated here. This is probably because most of preceramic polymers containing other elements are highly reactive and difficult to apply for the synthetic methodology described herein. As the more versatile and viable approach, the ceramization from an inorganic–organic hybrid gel, in which inorganic and organic species reside independently without any covalent bonds, has been proposed.^{47),48)} For example, the porous chromium-based ceramic (Cr_2O_3 , CrN and Cr_3C_2) monoliths can be fabricated from the porous gels composed of chromium oxyhydroxide, poly(acrylic acid) and urea, which play roles of chromium-, carbon- and nitrogen sources, respectively.⁴⁷⁾ The synthesis of the precursor hybrid gels is based on the epoxide-mediated sol–gel process, where a variety of metal salts are available for this method.^{10),49),50)} More sophisticated procedures might be ready to come out, which will further expand the frontiers of porous reduced ceramics in future.

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