Nanoscale

PAPER

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Cite this: Nanoscale, 2021, 13, 18173

Received 2nd August 2021, Accepted 29th September 2021 DOI: 10.1039/d1nr05052d

rsc.li/nanoscale

Introduction

As the energy consumption of human societies increases sharply, energy-related materials are attracting intensive attention from scientists, due to the concerns of sustainability.¹ In particular, among the energy-related issues, energy storage has become a hot research subject.² Recently, supercapacitors and batteries have been recognized as the main energy storage devices.³ While supercapacitors show fast charge–discharge kinetics and high power, their low energy storage capacity is a typical drawback. In comparison, while batteries show relatively high capacities, their charge–discharge processes are relatively slow. The energy storage capacity of supercapacitors can be significantly improved by employing redox-active species.⁴ The resultant pseudocapacitors can combine the merits of capacities and fast charge–discharge processes.

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Defect-rich CeO₂ in a hollow carbon matrix engineered from a microporous organic platform: a hydroxide-assisted high performance pseudocapacitive material[†]

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A microporous organic polymer (MOP) was utilized for the engineering of nanoparticulate CeO₂ in a hollow carbon matrix (H-C/CeO₂). After CeO₂ nanoparticles were incorporated into a hollow MOP platform (H-MOP) through the decomposition of cerium acetate, successive carbonization produced H-C/CeO₂. The redox feature of defective CeO₂ in a conductive carbon matrix induced promising pseudo-capacitive behavior. In particular, the H-C/CeO₂ showed excellent electrochemical performance in an alkaline electrolyte (KOH), due to the hydroxide ion-assisted redox behavior of defective CeO₂. H-C/CeO₂-3 with an optimized amount of CeO₂ showed specific capacitances of up to 527 (@0.5 A g⁻¹) and 493 F g⁻¹ (@1 A g⁻¹). Even at high current densities of 10 and 20 A g⁻¹, the H-C/CeO₂-3 maintained high capacitances of 458 and 440 F g⁻¹, respectively. After 10 000 cycling tests, the H-C/CeO₂-3 retained the 94–95% capacitance of the first cycle.

In this regard, there have been continuing studies on composite-based redox-active electrode materials.⁵ However, more exploration of efficient electrode materials is required.

CeO2 is a versatile material and has been utilized for various purposes including a heterogeneous catalyst or a solid support of the catalyst.⁶ As the prices of Ce and CeO₂ have consistently dropped, Ce-based materials have attracted great attention from scientists in academia and in industry.⁶ Basically, CeO₂ has a fluorite structure, in which each cerium is surrounded by eight oxygens.⁷ The oxygens in the CeO₂ are coordinated to four ceriums. Thus, the conventional oxidation state of ceriums in CeO₂ is +4. In comparison, the nanosized CeO₂ is an intriguing material.⁸ When the size of CeO₂ is reduced to nanoregimes, it becomes rich in oxygen defects, resulting in the generation of Ce(m) species. It has been known that the Ce(III) species of defective CeO₂ are redoxactive⁹ (Fig. 1). Thus, nanosized CeO₂ can be a candidate for pseudocapacitive materials. However, the systematic shape engineering of CeO2-based composite materials has been relatively less studied.¹⁰ To be utilized as pseudocapacitive energy storage materials, the size control of CeO₂ to nanoregimes is important. In addition, the defective CeO₂ can be incorporated into the conductive carbon matrix to improve its conductivity.

Recently, microporous organic polymers (MOPs) have emerged as new porous materials.¹¹ Various MOPs have been prepared by the coupling reactions of organic building

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[†]Electronic supplementary information (ESI) available: Additional characterization data of the H-MOP, H-MOP/CeO₂, P-CeO₂, H–C, H–C/CeO₂, and CeO₂. See DOI: 10.1039/d1nr05052d

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Fig. 1 Oxygen defects and Ce(III) species in nanoparticulate CeO₂.

blocks.¹¹ Moreover, the morphologies of MOPs could be controlled by various template methods.¹² For example, hollow MOPs have been prepared by silica-based template synthesis.^{12a} The hollow MOPs can be utilized as a platform material for the engineering of inorganic nanomaterials or composites.^{12a,13} Inorganic precursors can be incorporated into the micropores of MOPs. Then, the carbonization of MOPs with precursor materials can result in the inorganic nanomaterial-carbon composites.

In this work, we report the engineering of nanoparticulate CeO_2 in a hollow carbon matrix (H-C/CeO₂) using a hollow MOP platform (H-MOP) and electrochemical energy storage performance as an electrode material for pseudocapacitors.

Experimental

General information

Scanning electron microscopy (SEM) was conducted using a JSM6700F system. Transmission electron microscopy (TEM) studies and energy dispersive X-ray spectroscopy (EDS) were conducted using a JEOL 2100F system. N₂ sorption isotherm curves were obtained at 77 K using a Micromeritics ASAP2460 system. Pore size distribution diagrams were obtained by the density functional theory (DFT) method. Solid state ¹³C nuclear magnetic resonance (NMR) spectra were recorded at a CP-TOSS mode using a 500 MHz Bruker ADVANCE II NMR spectrometer. Infrared absorption (IR) and Raman spectra were recorded using a Bruker VERTEX 70 FT-IR system and a Renishaw inVia Raman Instrument, respectively. Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku MAX-2200 system. Electron paramagnetic resonance spectroscopy was conducted using EMX-plus equipment. X-ray photoelectron spectra (XPS) were recorded using a Thermo VG spectrometer. Thermogravimetric analysis (TGA) curves were obtained using a Seiko Exstar-7300 system. Inductively coupled plasma (ICP) analysis was conducted using an OPTIMA8300 system.

Synthesis of H-MOP, H-MOP/CeO₂, and P-CeO₂

As templates, silica spheres with an average diameter of 200 nm were prepared by the Stöber method.¹⁴ After ammonia solution (28–30% aqueous solution, 11 mL), ethanol (200 mL), and water (8 mL) were added to a 250 mL flask, the mixture

was stirred for 15 min. After tetraethylorthosilicate (TEOS, 14 mL) was added, the reaction mixture was stirred at room temperature for 18 h. After a mixture of hexane (400 mL) and methylene chloride (50 mL) was added, silica spheres were isolated by centrifugation, washed with water and ethanol, dried under vacuum, and calcined at 500 °C for 4 h.

For the preparation of H-MOP, silica spheres (0.50 g), (PPh₃)₂PdCl₂ (14 mg, 20 µmol), CuI (3.8 mg, 20 µmol), distilled triethylamine (TEA, 20 mL), and distilled toluene (20 mL) were added to a flame-dried 100 mL Schlenk flask under argon. After the mixture was sonicated for 30 min at room temperature, tetra(4-ethynylphenyl)methane¹⁵ (83 mg, 0.20 mmol) and 1,4-diiodobenzene (132 mg, 0.400 mmol) in TEA (20 mL) were added. The reaction mixture was stirred at 80 °C for 24 h. After being cooled to room temperature, the SiO₂@MOP was isolated by centrifugation, washed with a mixture of methanol (30 mL) and methylene chloride (5 mL) five times, and dried under vacuum. After the SiO₂@MOP was added to a mixture of water (7.5 mL), aqueous HF solution (48%, 7.5 mL), and methanol (25 mL) in a 50 mL Falcon tube, the mixture was stirred at room temperature for 3 h. Caution: The HF solution is very toxic and should be handled with specific gloves in a hood. Excess HF solution was quenched with NaOH solution. The H-MOP was isolated by centrifugation, washed with a mixture of methanol (30 mL) and methylene chloride (5 mL) five times, and dried under vacuum.

For the preparation of H-MOP/CeO₂-1, the H-MOP (25 mg) in ethanol (10 mL) was sonicated for 15 min in a Schlenk flask. After cerium acetate hydrate (50 mg, 0.16 mmol) in water (20 mL) was added, the reaction mixture was stirred at 80 °C for 24 h. After being cooled to room temperature, H-MOP/CeO₂-1 was isolated by centrifugation, washed with a mixture of ethanol (30 mL) and water (5 mL) three times, and dried under vacuum. For the preparation of H-MOP/CeO₂-2, H-MOP/CeO₂-3, and H-MOP/CeO₂-4, the same synthetic procedures of H-MOP/CeO₂-1 were applied except using cerium acetate hydrate of 0.10 (0.32 mmol), 0.20 (0.64 mmol), and 0.40 g (1.3 mmol), respectively. For the preparation of P-CeO₂, 0.20 g (0.64 mmol) of cerium acetate hydrate was used without using the H-MOP.

Synthesis of H-C, H-C/CeO₂, and CeO₂

For the synthesis of H-C, H-C/CeO₂-1, H-C/CeO₂-2, H-C/CeO₂-3, and CeO₂, the H-MOP, H-MOP/CeO₂-1, H-MOP/CeO₂-2, H-MOP/CeO₂-3, and P-CeO₂ were heated at 800 °C for 4 h in a furnace under argon.

Electrochemical studies

Electrochemical studies were conducted using CR2032 coin cell-type symmetric capacitors. To be used as working electrodes, H-C/CeO₂ (96 mg), carbon black (12 mg), polyvinylidene fluoride (PVDF, 12 mg), and *N*-methylpyrrolidone (NMP, 0.30 g) were ground in a mortar. After the slurry was coated on Ti foil (20 μ m, Wellcos Co.) using a doctor blade, it was dried at 90 °C for 1 h and at 110 °C for 18 h under vacuum. The circular working electrodes were prepared using a puncher (14 π). The loading amounts of working materials were found to be $1.21-1.45 \text{ mg cm}^{-2}$.

For the fabrication of symmetric coin cell-type capacitors, one of the working electrodes was loaded on a cap. After a circular filter paper (no. 20, Hyundai Micro Co.) that was prepared using a 19π puncher was loaded, it was wetted by electrolyte solution (0.15 g, 1 M H₂SO₄ or 6 M KOH). After the other working electrode was loaded, a space disc (Sus, 1T) and a spring were added. After the electrolyte solution (90 mg) was added, the other cap was loaded. Then, the coin cells were crimped. After a wetting time of 24 h, the electrochemical performance was investigated using an electrochemical workstation (WonATech ZIVE SPI). For the calculation of the specific capacitance (C_s) , the cell capacitance (C_{cell}) was obtained using the following equation: $C_{\text{cell}} = I/[(\Delta V / \Delta t) \times m], I = \text{current (A)},$ $\Delta V / \Delta t$ = the slope of discharge curves after the IR drop, and m = the total mass of electrode materials (g).¹⁶ The C_s of a single electrode corresponds to $4C_{cell}$.¹⁶

Results and discussion

Fig. 2 shows a synthetic scheme of the H-C/CeO₂ composites. First, the H-MOP platform was prepared by the template synthesis using silica spheres. A MOP was formed on the silica spheres through the Sonogashira coupling of building blocks, tetra(4-ethynylphenyl)methane¹⁵ and 1,4-diiodobenzene. Inner SiO₂ templates were etched through the treatment of aqueous HF solution. Then, nanoparticulate CeO2 materials were generated on the H-MOP through the decomposition of cerium acetate.¹⁷ With a fixed amount of H-MOP, we gradually increased the amount of Ce precursors from 0.16 mmol to 0.32 and 0.64 mmol, resulting in the formation of H-MOP/CeO₂-1, H-MOP/CeO₂-2, and H-MOP/CeO₂-3, respectively. Through the carbonization of H-MOP/CeO2-1, H-MOP/CeO2-2, and H-MOP/ CeO₂-3 at 800 °C under argon, H-C/CeO₂-1, H-C/CeO₂-2, and H-C/CeO₂-3 were obtained, respectively. As a control material, a hollow carbon material (H-C) without the loading of CeO₂ was prepared through the carbonization of the H-MOP. The nonhollow CeO_2 (denoted as CeO_2) was also obtained through the heat-treatment of CeO_2 (denoted as P-CeO₂) that was prepared without the use of the H-MOP template.

SEM and TEM studies confirmed the hollow structure of the H-MOP with an average diameter of 220 nm and an average shell thickness of 23 nm (Fig. S1 in the ESI†). As the amount of CeO₂ in H-MOP/CeO₂ increased, their shell thickness gradually increased (Fig. 3a–c). The TEM analysis revealed that the shell thicknesses of H-MOP/CeO₂-1, H-MOP/CeO₂-2, and H-MOP/CeO₂-3 increased to 28, 36, and 42 nm, with an increase of diameters to 228, 244, and 256 nm, respectively (Fig. 3d–f). The sizes of CeO₂ nanoparticles in all H-MOP/CeO₂ materials were quite uniform in the range of 5–6 nm (Fig. 3g–i). When the amount of a cerium precursor further increased to 1.28 mmol, a mixture of CeO₂ materials and H-MOP/CeO₂



Fig. 2 Synthetic schemes of H-MOP, H-C, H-MOP/CeO_2, and H-C/ CeO_2 materials.



Fig. 3 SEM images of (a) H-MOP/CeO₂-1, (b) H-MOP/CeO₂-2, and (c) H-MOP/CeO₂-3. TEM images of (d and g) H-MOP/CeO₂-1, (e and h) H-MOP/CeO₂-2, and (f and i) H-MOP/CeO₂-3.

(denoted as H-MOP/CeO₂-4) was obtained (Fig. S1 in the ESI[†]). The TEM analysis of P-CeO₂ revealed irregular materials with the aggregated CeO₂ nanoparticles (Fig. S1 in the ESI[†]).

The analysis of N₂ adsorption-desorption isotherm curves based on Brunauer–Emmett–Teller (BET) theory indicated that the H-MOP has a high surface area (SA) of 745 m² g⁻¹ and microporosity with a micropore volume ($V_{\rm mic}$) of 0.24 cm³ g⁻¹ (Fig. 4a, b and Table S1 in the ESI†). As the amount of CeO₂ increased in H-MOP/CeO₂-1, H-MOP/CeO₂-2, H-MOP/CeO₂-3, and H-MOP/CeO₂-4, their SAs decreased gradually to 534, 403, 282, and 152 m² g⁻¹ with a decrease of $V_{\rm mic}$ to 0.17, 0.12, 0.08, and 0.04 cm³ g⁻¹, respectively (Fig. 4a, b and S2 in the ESI†). In comparison, the SA and $V_{\rm mic}$ values of P-CeO₂ were found to be 54 m² g⁻¹ and 0.00 cm³ g⁻¹, respectively (Fig. S3 in the ESI†). The decreased $V_{\rm mic}$ values of H-MOP/CeO₂, compared



Fig. 4 (a) N₂ adsorption–desorption isotherm curves (77 K), (b) pore size distribution diagrams (the DFT method) of H-MOP and H-MOP/CeO₂. (c) Solid state ¹³C NMR spectrum of H-MOP. (d) IR spectra of H-MOP and H-MOP/CeO₂. (e) PXRD patterns, and (f) XPS spectra (Ce 3d orbital peaks) of H-MOP, H-MOP/CeO₂, and P-CeO₂.

The chemical structure of the H-MOP was characterized by solid state ¹³C-NMR and IR spectroscopy (Fig. 4c and d). In the ¹³C NMR spectrum of the H-MOP, the ¹³C peaks of internal alkynes and a benzyl carbon were observed at 80-95 and 63 ppm, respectively (Fig. 4c). In addition, aromatic ¹³C peaks appeared at 120, 130, and 145 ppm (Fig. 4c), matching with those of the MOP in the literature.¹⁸ In the IR spectrum of the H-MOP, the vibration peaks of aromatic C=C and C-H were observed at 1503 and 831 cm⁻¹, respectively.¹⁹ As the amount of CeO₂ increased in H-MOP/CeO₂, the intensities of the Ce-O vibration peaks²⁰ at 524 cm⁻¹ increased gradually with an increase of surface oxygen peaks at 1447 and 1516 cm⁻¹ (Fig. 4d).²⁰ ICP analysis indicated that the contents of incorporated CeO₂ in H-MOP/CeO₂-1, H-MOP/CeO₂-2, H-MOP/CeO₂-3, and H-MOP/CeO2-4 are 27.8, 41.6, 59.8, and 74.1 wt%, respectively.

Whilst the powder X-ray diffraction (PXRD) pattern of the H-MOP revealed the typical amorphous nature of MOPs in the literature,^{18,19} those of H-MOP/CeO₂ and P-CeO₂ confirmed the crystalline nature of CeO₂ (JCPDS# 81-0792) (Fig. 4e and S2 in the ESI†). The chemical surroundings of Ce in H-MOP/CeO₂ and P-CeO₂ were investigated by XPS studies (Fig. 4f). In the XPS spectra of H-MOP/CeO₂ materials and P-CeO₂, the 3d orbital peaks of Ce⁴⁺ species were observed at 882.3, 888.7, 898.3, 900.7, 907.1, and 916.6 eV, matching with those of CeO₂ materials in the literature.²¹ In comparison, those of the Ce³⁺ species mainly appeared at 884.7 and 903.1 eV (Fig. 4f and S4 in the ESI†).²¹ Thermogravimetric analysis (TGA) indicated that the H-MOP in the H-MOP/CeO₂ started to decompose at ~285 °C (Fig. S5 in the ESI†).

The morphologies of the H-C, H-C/CeO₂, and CeO₂ were also investigated by TEM and SEM studies (Fig. 5 and S6 in the ESI[†]). The H-C, H-C/CeO₂-1, H-C/CeO₂-2, and H-C/CeO₂-3 retained the original hollow morphologies, diameters, and shell thicknesses of the H-MOP and H-MOP/CeO2-1, H-MOP/ CeO₂-2, and H-MOP/CeO₂-3, respectively (Fig. 5a-d and S6 in the ESI[†]). The diameter and shell thickness of H-C were found to be 220 nm and 23 nm, respectively (Fig. 5a). As the amount of CeO2 in H-C/CeO2 increased, the diameters of H-C/CeO₂-1, H-C/CeO₂-2, and H-C/CeO₂-3 gradually increased to 225, 240, and 255 nm, respectively (Fig. 5b-d and g-i). The shell thicknesses of H-C/CeO₂-1, H-C/CeO₂-2, and H-C/ CeO₂-3 also increased to 28, 38, and 47 nm, respectively (Fig. 5b-d and g-i). Even after carbonization of H-MOP/CeO₂, the interconnected CeO2 materials in H-C/CeO2 maintained their nanoparticulate feature with a size range of 5-6 nm (Fig. 5g-i and S7 in the ESI[†]). The elemental mapping images of H-C/CeO₂-3 based on energy dispersive X-ray spectroscopy confirmed the homogeneous distribution of CeO2 materials over H-C supports (Fig. S7 in the ESI[†]). In the case of H-C/CeO₂-4 obtained through the carbonation of H-MOP/ CeO₂-4, its SEM and TEM images showed a mixture of H-C/ CeO_2 and free CeO_2 materials (Fig. 5e and S6 in the ESI[†]).

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Fig. 5 TEM images of (a) H-C, (b and g) H-C/CeO₂-1, (c and h) H-C/CeO₂-2, (d and i) H-C/CeO₂-3, (e) H-C/CeO₂-4, and (f) CeO₂. Refer to Fig. S6 in the ESI† for the lower magnification SEM images of H-C, H-C/CeO₂, and CeO₂.

The CeO₂ obtained by the heat-treatment of P-CeO₂ showed irregular aggregates with a broad size range of 200 nm-1 μ m (Fig. 5f and S6 in the ESI†).

The H-C and H-C/CeO₂ showed high and significant SAs (Fig. 6a, b and Table S1 in the ESI[†]). The H-C showed an enhanced SA of 1017 m² g⁻¹ and $V_{\rm mic}$ of 0.32 cm³ g⁻¹, compared with those of the H-MOP (Fig. 4a and 6a). As the CeO₂ was incorporated into the H-C, the SAs of the resultant H-C/CeO₂-1, H-C/CeO₂-2, H-C/CeO₂-3, and H-C/CeO₂-4 decreased gradually to 537, 425, 279, and 159 m² g⁻¹ with the decreased $V_{\rm mic}$ values of 0.17, 0.16, 0.10, and 0.05 cm³ g⁻¹, respectively (Fig. 6a, b, S2 and Table S1 in the ESI[†]). In comparison, the CeO₂ showed a SA of 73 m² g⁻¹ and a $V_{\rm mic}$ of 0.00 cm³ g⁻¹ (Fig. S3 in the ESI[†]).

According to the PXRD studies, whilst the H-C is amorphous, the crystallinity of CeO₂ in the H-C/CeO₂ improved significantly (Fig. 6c), compared with those of H-MOP/CeO₂ (Fig. 4e). The main XRD peaks of H-C/CeO₂ and CeO₂ were observed at 2θ values of 28.6, 33.0, 47.5, and 56.4°, corresponding to the (111), (200), (220), and (311) crystalline planes of face-centered cubic CeO₂ (JCPDS# 81-0792) (Fig. 6c and S2 in the ESI†). Electron paramagnetic resonance (EPR) spectroscopy showed the existence of paramagnetic Ce³⁺ species in the H-C/CeO₂ materials (Fig. S8 in the ESI†).²² In the XPS spectra of H-C/CeO₂ and CeO₂, the typical 3d orbital peaks of Ce⁴⁺ were observed at 882.5, 888.9, 898.5, 900.9, 907.3, and 916.8 eV (Fig. 6d).²¹ The unique 3d orbital peaks of Ce³⁺ species mainly appeared at 884.9 and 903.3 eV, respectively.²¹



Fig. 6 (a) N₂ adsorption–desorption isotherm curves (77 K) and (b) pore size distribution diagrams (based on the DFT method) of H-C and H-C/CeO₂. (c) PXRD patterns (d) XPS spectra (3d orbital peaks of Ce), (e) IR spectra, and (f) Raman spectra of H-C, H-C/CeO₂, and CeO₂.

increase of CeO₂ contents in H-C/CeO₂ and CeO₂, indicating that the oxygen defects of CeO₂ nanoparticles originate from the incomplete surface structures. The Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratios in H-C/CeO₂-1, H-C/CeO₂-2, H-C/CeO₂-3, and CeO₂ were analyzed to be 0.54, 0.49, 0.38, and 0.30, respectively (Fig. S4 in the ESI[†]).

Whilst the IR spectrum of the H-C did not show specific vibration peaks, those of H-C/CeO₂ and CeO₂ showed only Ce–O vibration peaks at 530 cm⁻¹ (Fig. 4d and 6e), indicating complete carbonization. In the Raman spectrum, the typical carbon D and G band peaks of H-C and H-C/CeO₂ were observed at 1337 and 1565 cm⁻¹, respectively, with a gradual increase of I_D/I_G values from 0.98 (H-C) to 1.03 (H-C/CeO₂-1), 1.09 (H-C/CeO₂-2), and 1.09 (H-C/CeO₂-3) (Fig. 6f). The ICP analysis indicated that the contents of CeO₂ in the H-C/CeO₂-1, H-C/CeO₂-2, H-C/CeO₂-3, and H-C/CeO₂-4 are 28.8, 45.5, 60.9, and 75.2 wt%, respectively.

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Next, the energy storage performance of H-C/CeO₂ was studied. Using working electrodes bearing H-C/CeO₂, symmetric coin cell-type capacitors were assembled. As control materials, the CeO₂ and H-C were tested. Fig. 7–9, S9–11, and Table S1 in the ESI[†] summarize the results. First, we found that the H-C/CeO₂ showed clearly different electrochemical behaviors depending on electrolytes (Fig. 7 and 8). The electrochemical responses of H-C/CeO₂ were significantly enhanced in an aqueous KOH electrolyte, compared with those in aqueous H₂SO₄ (Fig. 7a and b). In aqueous H₂SO₄, as the amount of CeO₂ in H-C/CeO₂ increased, the electrochemical responses were reduced in the order of H-C/CeO₂-1 > H-C > H-C/CeO₂-2 > H-C/CeO₂-3 > H-C/CeO₂-4 > CeO₂ (Fig. 7a and





Fig. 8 Nyquist plots of H-C, H-C/CeO₂, and CeO₂ in coin cell-type capacitors with aqueous (a) H_2SO_4 and (b) KOH electrolytes. (c) A hydroxide ion-assisted redox reaction of Ce(III) species in defective CeO₂ in an aqueous KOH electrolyte.



Fig. 9 (a) Charge–discharge cycling performance of the coin cell-type capacitors of $H-C/CeO_2-3$ in an aqueous KOH electrolyte and a TEM image of $H-C/CeO_2-3$ retrieved after 10 000 cycles. (b) Nyquist plots and (c) XPS spectra (Ce 3d orbital peaks) of $H-C/CeO_2-3$ before and after 10 000 cycles (refer to Fig. S4 and S12 in the ESI†).

Fig. 7 (a) Cyclic voltammograms (scan rate: 100 mV s⁻¹), (c) chargedischarge profiles (current density: 0.5 A g⁻¹), and (e) rate performance of H-C, H-C/CeO₂, and CeO₂ in coin cell-type symmetric capacitors with an aqueous H₂SO₄ electrolyte. (b) Cyclic voltammograms (scan rate: 100 mV s⁻¹), (d) charge-discharge profiles (current density: 0.5 A g⁻¹), and (f) rate performance of H-C, H-C/CeO₂, and CeO₂ in coin celltype symmetric capacitors with an aqueous KOH electrolyte.

S9–11 in the ESI[†]). In comparison, as the amount of CeO_2 in H-C/CeO₂ increased, the electrochemical responses increased gradually in an aqueous KOH electrolyte and then decreased

in the order of H-C/CeO₂-3 > H-C/CeO₂-2 > H-C/CeO₂-1 > H-C > H-C/CeO₂-4 > CeO₂ (Fig. 7b and S9–11 in the ESI \dagger).

In the charge-discharge profiles, whilst the H-C/CeO2 showed capacitive behavior in aqueous H₂SO₄, it showed a pseudocapacitive feature with a redox characteristic in aqueous KOH (Fig. 7c and d). At a current density of 0.5 A g^{-1} , the H-C, H-C/CeO₂-1, H-C/CeO₂-2, H-C/CeO₂-3, H-C/CeO₂-4 and CeO₂ in aqueous H₂SO₄ showed capacitances of 177, 221, 109, 60, 30, and 0.37 F g^{-1} , respectively (Fig. 7e). In comparison, at a current density of 0.5 A g⁻¹, the H-C, H-C/CeO₂-1, H-C/CeO₂-2, H-C/CeO₂-3, H-C/CeO₂-4, and CeO₂ in aqueous KOH showed capacitances of 195, 296, 415, 527, 75, and 4.5 F g⁻¹, respectively (Fig. 7f). The sharply decreased capacitance of H-C/CeO₂-4 indicates that excess CeO₂ results in poor electrochemical behavior, due to poor conductivity (Fig. S9-11 and Table S1 in the ESI[†]). Thus, the H-C/CeO₂-3 in the aqueous KOH electrolyte showed the best performance, displaying capacitances of 493, 487, and 472 F g^{-1} at current densities of 1, 2, and 4 A g^{-1} , respectively (Fig. 7f and S11 in the ESI[†]). Even at high current densities of 10 and 20 A g⁻¹, the H-C/CeO₂-3 retained capacitances of up to 458 and 440 F g^{-1} , respectively.

According to the electrochemical impedance spectroscopy (EIS), whilst the H-C showed a conductive feature in aqueous H₂SO₄ and KOH electrolytes, the charge transfer resistances (R_{ct}) of H-C/CeO₂ increased gradually with an increase in the amount of CeO₂ (Fig. 8a, b and S10 in the ESI[†]). The H-C/ CeO₂-1, H-C/CeO₂-2, H-C/CeO₂-3, and H-C/CeO₂-4 exhibited R_{ct} values of 38, 42, 73, and 103 Ω , respectively, in aqueous H₂SO₄ (Fig. 8a). In comparison, the H-C/CeO₂-1, H-C/CeO₂-2, H-C/ CeO₂-3, and H-C/CeO₂-4 showed improved conductivities in aqueous KOH with R_{ct} values of 3.3, 7.1, 10, and 25 Ω , respectively (Fig. 8b). The CeO₂ also showed a significantly lower R_{ct} of 35 Ω in aqueous KOH, compared with that of 156 Ω in aqueous H₂SO₄. These observations indicate that the redox behavior of CeO₂ can be enhanced in aqueous KOH, compared with that in aqueous H_2SO_4 . We suggest that the redox activities⁹ of Ce³⁺ in defective CeO₂ can be assisted by the hydroxide ions in aqueous KOH through coordination to the oxidized Ce^{4+} species (Fig. 8c). It is noteworthy that the hydroxideassisted redox behavior of RuO2 was reported in the literature.23

The charge–discharge cycling performance of coin cell-type capacitors of H-C/CeO₂-3 was studied in an aqueous KOH electrolyte (Fig. 9a). At the 10 000th cycle, the H-C/CeO₂-3 maintained a capacitance of 470 F g⁻¹ at a current density of 1 A g⁻¹, corresponding to the 95.3% capacitance of the first cycle. At a current density of 10 A g⁻¹, the coin cell-type capacitor of H-C/CeO₂-3 showed a capacitance of 426 F g⁻¹ at the 10 000th cycle, corresponding to the 94.7% capacitance of the first cycle. After 10 000 cycles, the H-C/CeO₂-3 maintained an $R_{\rm ct}$ of 14 Ω , compared with the original $R_{\rm ct}$ of 10 Ω (Fig. 9b). To investigate the morphological and chemical changes of a working material, the H-C/CeO₂-3 was retrieved from the symmetric coin cell-type capacitor after 10 000 cycling tests. As shown in the TEM images in Fig. 9a and S12 in the ESI,† the original structure of H-C/CeO₂-3 was completely retained after 10 000

cycles. In the XPS analysis, whilst the $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ ratios of H-C/CeO₂-3 were slightly changed from 0.38 (before cycles) to 0.36 (after 10 000 cycles), overall, the original chemical surroundings of the Ce species of H-C/CeO₂-3 were retained (Fig. 9c and S4 in the ESI†).

Recently, MOPs, especially conjugated microporous polymers (CMPs), have been applied as energy storage materials for supercapacitors.^{11,24} Whilst the MOPs or CMPs themselves were applied as electrode materials of supercapacitors, they could be utilized in the engineering of carbon-based electrode materials.²⁵ For example, Cooper et al. reported the N-doped and carbonized CMP showing capacitances of up to 164 F g^{-1} $((a) 1 A g^{-1})$.^{25a} Recently, our research group reported the synthesis of N-doped hollow carbon boxes from click-based MOPs, displaying capacitances of up to 286 F g^{-1} (@1 A g^{-1}).^{25d} In addition, recently, CeO₂-based electrode materials have been reported for supercapacitors (Table S2 in the ESI[†]).^{10,26,27} First, nanoengineered CeO₂ materials have been studied as electrode materials for supercapacitors.¹⁰ For example, CeO_2 nanocubes,^{10*a*} porous CeO_2 ,^{10*b*} and {100} faceted CeO₂ nanocrystals^{10d} showed capacitances of up to 88.71 F g^{-1} (@5 A g^{-1}), 134.6 F g^{-1} (@1 A g^{-1}), and 339.5 F g^{-1} ((a)1 A g⁻¹), respectively. Second, metal-doped CeO₂ nanomaterials were engineered,²⁶ showing capacitances of 274.3-328 F g^{-1} (@0.5 A g^{-1}). Finally, CeO₂/carbon compositebased electrode materials such as CeO₂/graphene and CeO₂/ CNT composites were engineered,²⁷ displaying capacitances of up to 455.7 F g^{-1} (@1 A g^{-1}). In comparison, the electrochemical performance of the H-C/CeO2-3 in this work with capacitances of 527 F g^{-1} (@0.5 A g^{-1}), 493 F g^{-1} (@1 A g^{-1}), and 458 F g^{-1} (@10 A g^{-1}) is superior or comparable to those of recently reported CeO2-based electrode materials in the literature (Table S2 in the ESI[†]).^{10,26,27} The excellent electrochemical performance of H-C/CeO2-3 is attributable to the promising redox behavior⁹ of nanoparticulate CeO₂ materials and the enhanced conductivities by the carbon materials. In particular, we suggest that the hollow structure of H-C/CeO₂-3 can induce the efficient utilization of the electrochemically active species and the facile diffusion of the electrolyte solution into electrode materials.28

Conclusions

This work shows that the potential pseudocapacitive feature of defective CeO₂ nanoparticles could be realized through the systematic engineering of hollow CeO₂-carbon composites based on MOP chemistry. Using the H-MOP as a microporous platform material, the nanoparticulate CeO₂ could be incorporated into a hollow carbon matrix. The electrochemical responses of H-C/CeO₂ were enhanced in an aqueous alkaline electrolyte. We suggest that the hydroxide ions facilitate the redox behaviors of the defective CeO₂ through coordination to the oxidized Ce⁴⁺ species. The optimized H-C/CeO₂ showed promising energy storage performance with capacitances of up to 527 ($(@0.5 \text{ A g}^{-1})$, 493 ($(@1 \text{ A g}^{-1})$, and 458 F g⁻¹ ($(@10 \text{ A g}^{-1})$). In

addition, the H-C/CeO₂ showed excellent cycling performance for 10 000 cycles. We believe that more various hollow composite-based electrode materials can be engineered using a morphology-controlled MOP as a platform material.

Author contributions

S. U. Son: conceptualization, supervision, writing original draft, and review & editing. C. W. Kang, Y. Myung, and S. M. Lee: investigation and formal analysis. H. J. Kim: formal analysis and supervision.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant (No. 2020R1A2C200431011) funded by the Korean government (MSIT).

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