Design of a Rechargeable Fuel-Cell Battery with Enhanced Performance and Cyclability

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Electrochemical devices integrating a fuel cell with a hydrogen storage medium are able to function as secondary batteries. Batteries incorporating a partially oxidized carbon cathode with a RuO2/C cathode exhibit excellent reversibility, but their performance is not yet sufficient for secondary battery applications. This is due to excessive oxygenation of the anode, degradation of the cathode and the excess weight of the electrolyte membrane. In the present work, we addressed these challenges through various improvements in the design of a rechargeable proton-exchange membrane battery. These included coating the surface of a significantly oxygenated carbon anode (O/C atomic ratio 0.131) with carbon black nanoparticles, nanocrystallization of a carbon-free RuO2 cathode (avg. crystallite size 1.1 nm) and the synthesis of an inorganic-organic composite electrolyte membrane. As a result of these optimizations, coulombic efficiencies of over 95% were achieved during charge/discharge over the voltage range of 0.0–1.5 V at 75 °C. The resulting device exhibited an initial capacity of 330 mAh g−1 and was stable over 300 cycles, with maximum energy and power densities of 47 Wh kg−1 and 1114 W kg−1, respectively.

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Hydrogen is a promising medium for the storage and supply of electricity through water-electrolysis/fuel-cell operation.1,2 The primary application of hydrogen in this context would be to store surplus power when the quantity of electricity produced by natural energy sources exceeds that required by a consumer.3–5 Rechargeable batteries offer a means of storing and supplying this energy when the quantity of electricity produced by natural energy sources exceeds that required by a consumer.6–8 The key technology necessary for such devices is hydrogen storage, which is currently accomplished via liquefaction and compression of the gas or by the physical or chemical adsorption of hydrogen atoms or molecules in/on materials such as metal or organic chemical hydrides.9,10 However, an energy input is required for these processes that in turn increases the overall cost. Furthermore, the hydrogen tanks and lines employed in such systems negatively impact their volumetric energy density.

To mitigate these problems, rechargeable fuel-cell batteries (RFCBs) containing a hydrogen storage medium have been proposed.11–13 During the operation of such batteries, hydrogen production, storage, supply and utilization processes must be conducted at the anode under the standard operational conditions of the cell, such as between room temperature and 80 °C and at ambient pressure. In this context, oxygen-functionalized microporous carbons (MPCs) are promising hydrogen storage media, due to their efficient reversibility.11 The redox pair between carbonyl (C=O) and phenol (C–OH) groups is one of the most important hydrogen carrier sites in such carbon anodes. The origin of this redox reaction is ascribed to the following equilibrium reaction between the two functional groups:14

\[ \text{C} = \text{O} + \text{H}^+ + e^- \rightleftharpoons \text{C} - \text{OH} \]  

[1]

This reaction determines the electrical capacity of an RFCB, because the cathode operates using oxygen and water vapor, both of which are abundant in air; as in the following equation.

\[ \frac{1}{2}\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + e^- + \frac{1}{2}\text{O}_2 \]  

[2]

However, unlike other batteries, no distinct voltage plateau is observed during galvanostatic discharge. This is attributable to the dependence of the redox potential of Reaction 1 on the species providing the carboxyl/phenol groups. Various types of carboxyl/phenol groups are present on the surfaces of oxygenated MPCs.15 These functional groups are also electrochemically active over a wide potential window of 0–1.5 V.16,17 therefore, such redox reactions cannot provide the battery a fixed open-circuit voltage (OCV). As a result, RFCBs function as power sources with energy densities of 2.5–13.8 Wh kg−1 and power densities of 46.4–296.3 W kg−1 (normalized according to the mass of the entire cell).13 Nevertheless, the performance of RFCBs is lower than those of other types of batteries and fuel cells, largely because of the low electrical capacity (73–202 mAh g−1) of the anode, as well as because of the degradation (at least 20% after 300 cycles) of the cathode, especially at high charge voltages, and the highly dense (90 mg cm−2) electrolyte membrane. The first problem is caused by the formation of carbonyl groups (C=O) on the external surface of the highly oxygenated MPC anode; these carbonyl group have little reversible redox ability and are also one of the least conductive functional groups.18,19 The second issue is due to corrosion of the carbon support for the RuO2 catalyst at the cathode during charging.15 Finally, mass becomes a problem because the electrolyte accounts for approximately 70–80% of the total cell weight. These challenges could potentially be mitigated by coating the anode with highly conductive carbon nanoparticles, thus decreasing the resistive loss and/or overpotential of the anode, and enhancing the anode potential accumulated by charging the cell. Alternatively, the use of a cathode without a carbon support could also contribute to improved cyclability of the cell, although the trade-off between resistance and stability must be addressed. Finally, the fabrication of a thinner electrolyte membrane will be necessary to realize a lightweight device, and inorganic-organic composites are promising candidates for such membranes. In the work reported herein, the validity of each of these approaches was examined as a means of improving an RFCB operating from room temperature to 75 °C with a voltage range of 0.0–1.5 V.

Experimental

Materials.—MPC anodes were synthesized according to a previously reported procedure.15 The porous carbon (Maxsorb MSC-30: surface area 2433 m2 g−1, micropore volume 1.60 cm3 g−1, mesopore volume 0.87 cm3 g−1) was purchased from Kansai Coke and Chemicals. This material was subsequently modified as follows. First, 1 g of the carbon was stirred in 50 mL 24 wt% HNO3 at 50 °C for 90 h. After filtering and washing, the product was dried under vacuum at 120 °C for 6 h. In a second step, 0.19 g of the treated carbon and 0.01 g carbon black (CB) (Asahi Carbon CB1) were suspended in approximately 20 mL ethanol and then mixed in a mortar until the ethanol was almost completely evaporated. This mixing procedure was repeated three times to ensure good coverage of the carbon surfaces with the CB. After drying at 75 °C for 2 h, the product (1.0 g) was dispersed.

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with a small amount (ca. 0.1 g) of 105% H₃PO₄ ionomer (Aldrich) in a mixer (Thinky AR-100) for 30 min. (The H₃PO₄ concentration is finally decreased to ca. 80%, due to the adsorption of water vapor from atmospheric air.) The obtained slurry was deposited on the surface of carbon fiber paper (Toray TGP-H-090). The anode loading (approx. 1–6 mg) was adjusted according to the desired electrode thickness (0.095–0.436 mm).

A RuO₂ cathode was prepared from RuCl₃ (ruthenium(III) chloride n-hydrate, Wako) via the following procedure. First, 1 g RuCl₃ was dissolved in 50 mL deionized water, after which 0.3 M NaOH was added dropwise with stirring at room temperature to increase the pH of the solution to 7. After a further 15 h at ambient temperature, the precipitate was filtered and washed with deionized water until no chloride ions were detected in the rinse water, as determined by a spectrophotometer (JASCO MRS-1000) with a wavelength 3.5 mW laser.

The resulting slurry was dried at 75°C for 4 h. After addition of the 105% H₃PO₄ ionomer, the resulting electrode slurries were coated onto carbon fiber paper in a similar manner to the procedure used in making the anode. The cathode loading was adjusted to approximately 10 mg (thickness 0.214 mm).

Sn₀.₉₅P₅O₁₇ (SIPO) was selected as the electrolyte material because, according to previous reports, it has a proton conductivity of approximately 0.05 S cm⁻¹ and does not require excessive humidification. Two electrolyte membranes were prepared according to previously reported procedures. One was a composite membrane consisting of 96.2 wt% SIPO and 3.8 wt% polytetrafluoroethylene (PTFE) with a thickness of approximately 250 μm. The other was a composite membrane composed of 80 wt% SIPO and 20 wt% sulfonated polystyrene-b-poly(ethylene/butylene)-b-polystyrene (sSEBS) with various thicknesses between 37 and 133 μm. The SIPO-sSEBS composite membrane was prepared as follows. A mixture of 80 wt% toluene (9.2 g) and 20 wt% iso-butanol (2.3 g) was used to dissolve a quantity of sSEBS (Kuraray Co., Ltd., 1.0 g). Subsequently, 4 g of powdered SIPO was added to the solution and the mixture was ground in a planetary ball mill at 150 rpm over 12 h. The resulting slurry was cast onto a polyethylene terephthalate (PET) substrate using a doctor blade and dried, first under ambient conditions for 2 h and then at 120°C in air for 4 h, to completely remove the solvent. Finally, the membrane was peeled off and cut into test samples of various sizes. The SIPO-PTFE composite membrane was employed as the electrolyte in anode and cathode half-cells, while the SIPO-sSEBS composite membrane was examined as the electrolyte for RFCBs (Fig. S1 in Supplemental Information).

Characterization.—The O/C atomic ratios of carbon samples were determined using energy-dispersive X-ray (EDX) spectroscopy in conjunction with a scanning electron microscope (SEM; JEOL JSM-6610A) system. The quantities of functional groups were determined according to the method suggested by Boehm. NaOH and NaHCO₃ were used as reaction reagents for measurements of the total number of acidic groups (phenol and carboxyl (COOH)) and the number of carboxyl groups, respectively. Attenuated total reflection (ATR) Fourier transform infrared (FT-IR) spectra were recorded on a Varian-7000 instrument. The C 1s and O 1s chemical charge states were analyzed using X-ray photoelectron spectroscopy (XPS; VG Escallab220i-XL). The pore characteristics of samples were assessed by N₂ adsorption at liquid N₂ temperature (Bel Japan BELSORP18PLUS-HT) and specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method.

The fine structures of the RuO₂ samples were observed using Cs-corrected transmission electron microscopy (TEM; JEOL-200 kV) with atomic resolution. X-ray diffraction (XRD) patterns were collected using a diffractometer (Rigaku Miniflex II) operated at 45 kV and 20 mA with Cu Kα radiation (λ = 1.5432 Å). Raman spectra were acquired using a spectrophotometer (JASCO MRS-1000) with a 532 nm single wavelength 3.5 mW laser.

The cross-sectional and surface morphologies of the membrane samples were analyzed by SEM. Conductivity measurements were performed in non-humidified air at temperatures between 25 and 100°C. Impedance spectra were recorded using an impedance analyzer (Solartron SI 1260) and an electrochemical interface (Solartron 1287) in the frequency range of 10–10⁶ Hz with an AC amplitude of 10 mV. The conductivities and area-specific ohmic resistances of the membrane samples were estimated from the intercepts of the impedance line and the real axis in Nyquist plots.

Electrochemical measurements.—Electrochemical devices were fabricated by sandwiching the electrolyte membrane between two electrodes (0.5 cm²). The oxygenated carbon electrode was attached to a stainless steel current collector and then sealed using thermally and chemically resistant PTFE tape (Nitto Denko). The RuO₂ electrode was supplied with atmospheric air at a flow rate of 30 mL min⁻¹. In situ cyclic voltammetry (CV) measurements of the oxygenated carbon and RuO₂ working electrodes were conducted in the three-electrode mode, using a commercially available Pt/C electrode (40 wt% Pt, ElectrocChem) as both the counter and reference electrodes. For both measurements, the reference electrode was exposed to atmospheric air with a relative humidity in the vicinity of 50%. Voltammograms for the oxygenated carbon electrode were obtained using a cell in which atmospheric air (30 mL min⁻¹) was supplied to the counter electrode, while those for the RuO₂ electrode were recorded with a cell in which hydrogen (30 mL min⁻¹) was supplied to the counter electrode. The scan rate in these trials was in the range of 10–50 mV s⁻¹. Impedance spectra of the working electrode were also acquired in the three-electrode mode. The ohmic and polarization resistances were assessed using an impedance analyzer and the electrochemical interface in the frequency range of 0.1–10⁶ Hz with an AC amplitude of 10 mV. In contrast, battery and fuel cell tests employing an RFCB with an oxygenated anode and a RuO₂ cathode were performed via the four-probe method. During battery tests, the electrical capacity was obtained from galvanostatic charge-discharge measurements with the current density and charge voltage in the range of 40–100 mA cm⁻² and at 1.5 V, respectively, unless otherwise stated. The voltage during charge and discharge was monitored using an impedance analyzer and the electrochemical interface. The energy density was calculated by integrating the area under the voltage-time curve during discharge, giving a value that was then normalized according to the total weight of the membrane and electrolyte active materials. The power density was also estimated by dividing the energy density by the discharge time. In the case of the fuel cell tests, the current-voltage and current-power density curves were obtained by charging the cell to 1.5 V at 40 mA cm⁻², followed by discharging the cell at a current-sweep rate of 10 mA s⁻¹. The power density was normalized with respect to the area, total weight and total volume of the cell.

Results and Discussion

Characterization and electrochemical studies of anode materials.—In this work, the MPC was treated with 24 wt% HNO₃ at 50°C for 90 h to form carbonyl groups. As a result of this treatment, an increase in the O/C atomic ratio from 0.010 to 0.131 was observed using EDX spectroscopy. This ratio is higher than that (0.096) for the MPC that exhibited the best anode performance in a previous study, in which the MPC treatment was conducted with the same HNO₃ solution as above but at room temperature. However, it should be noted that the O/C atomic ratios determined from XPS were higher than those calculated from the EDX data, and the extent of this discrepancy was more significant in the case of the MPC prepared in this study. This suggests that the MPC was more highly oxygenated on its external surface compared to its interior, especially when applying the more severe acid treatment conditions. The IR spectra of MPCs with O/C atomic ratios of 0.096 and 0.131 confirmed the presence of carbonyl groups (absorption at 1720 cm⁻¹) in addition to hydroxyl groups (absorption in the 3000–3600 cm⁻¹ range) and carboxyl groups (absorption at 1580 cm⁻¹) in addition to hydroxyl groups (absorption in the 3000–3600 cm⁻¹ range) and carboxyl groups (absorption at 1580 cm⁻¹).
Figure 1. Characterization of MPCs (with different O/C atomic ratios), CB and a CB-coated MPC. (a) FT-IR spectra of MPCs, (b) XPS peak intensities of MPCs, (c) N2 adsorption/desorption isotherms of an MPC with an O/C atomic ratio of 0.131 and of CB, at 77 K and (d) an SEM image of a CB-coated MPC.

COOH (288.9 eV) peaks on the surfaces of the oxygenated MPCs (Fig. 1b). Another important result in Fig. 1a is the abrupt increase in the intensity of the C–O stretching band (1190 cm\(^{-1}\)) of the carboxyl group at an O/C atomic ratio of 0.131, demonstrating that a number of carbonyl groups were oxidized to carboxyl groups in this sample, as a result of the severe acid treatment. This is supported by the large increase in the number of carboxyl groups on the MPC surface (to 1.155 mEq g\(^{-1}\)) at an O/C atomic ratio of 0.131 (Fig. S2).

The porosities of the MPC with an O/C atomic ratio of 0.131 and of the CB were independently investigated by N2 adsorption-desorption isotherm measurements before the materials were mixed (Fig. 1c). The MPC and CB generated types I and II isotherms, respectively, which are characteristic of microporous and non-porous materials. Consequently, there was a large difference in the BET specific surface areas of the two samples; 1668 and 48 m\(^2\) g\(^{-1}\) for the MPC and CB, respectively. Moreover, the CB had a significantly lower total number of acidic groups than the MPC (Fig. S2). Based on these data, it is believed that the electrical capacity of the CB was negligibly lower than that of the MPC. The capacitive characteristics of MPCs with different O/C atomic ratios and of an MPC coated with the CB were assessed using the three- or two-electrode methods. The in situ CV profiles were found to be significantly affected by the MPC species (Fig. 2a). In the case of the CB-free MPCs, the slope angle of the CV curve approached 45° relative to the x-axis with increasing O/C atomic ratio from 0.010 to 0.096, but greatly decreased at an O/C atomic ratio of 0.131. These MPCs showed a similar change in capacitance with variations in the O/C atomic ratio; the largest integrated area was obtained at an O/C atomic ratio of 0.096 rather than 0.131. Both these phenomena are attributable to faradaic reactions on the surfaces of the electrodes, such that the rectangular shape of the CV curve is distorted by the voltage drop and the capacitance in the CV curve is enhanced by an increase in the hydrogen storage capacity. Only the MPC with an O/C atomic ratio of 0.131 deviated from these patterns, due to the large internal resistance of this specimen (Fig. 2b). However, this deviation was eliminated by coating the MPC with a small quantity (5 wt%) of CB. The resultant MPC sample showed the largest capacitance (Fig. 2a), attributed to decreases in both the ohmic and polarization resistances (Fig. 2b). The reduced ohmic resistance is considered to result from the improved electrical contact between the MPC particles. It is also reasonable to conclude that the current collection ability of the electrode is enhanced, contributing to the decrease in the polarization resistance.

The galvanostatic discharge profiles of cells using the above MPCs as anodes were obtained by charging to 1.0 V with a current density of 10 mA cm\(^{-2}\) at room temperature (Fig. 2c and Fig. S3). It was also evident that the cells with the oxygenated MPC anodes typically yielded slightly convex-upward curves, as opposed to the concave-downward curve obtained from the cell with the untreated MPC anode (Fig. S3). This convex shape may be related to the carbonyl/phenol redox reaction that occurs at the anodes, as will be discussed in the next paragraph. Subsequent experimental trials were conducted using the CB-coated MPC anode.

To obtain additional insight into these results, in situ CV measurements were conducted over the potential range of 0.0 − 2.0 V (versus air reference) at a slower scan rate of 10 mV s\(^{-1}\) (Fig. 2d). Several pairs of cathodic/anodic redox bands appeared in the ranges of −0.5 − 1.0 V, −1.0 − 1.5 V and −1.5 − 1.9 V, and the validity of this result was verified by CV measurements using 1,4-benzoquinone...
profiles of a cell with an MPC anode charged between 0.50 and 1.75 V. From these results, it is apparent that a charging voltage of 1.5 V provides the best balance between efficiency and capacity for a cell incorporating the present MPC anode.

Characterization and electrochemical studies of cathode materials.—Both RuO$_2$ and IrO$_2$ have been intensively studied as pseudocapacitors because of their high specific capacitances.$^{36,37}$ These materials have also been shown to represent important replacements for platinum in electrolysis and fuel cells.$^{38,39}$ We conducted preliminary tests using these commercially available materials as cathode materials for RFCBs and found that RuO$_2$ showed a higher cathode performance than IrO$_2$. Subsequently, nanocrystalline RuO$_2$ was synthesized from RuCl$_3$ in our own laboratory and compared to the commercial RuO$_2$, air batteries.

Evidence supporting the above theory is provided by the discharge profiles of a cell with an MPC anode charged between 0.50 and 1.75 V with a current density of 10 mA cm$^{-2}$ (Fig. 2d), and these plateau values were close to the values that would be predicted from the respective redox potentials. Considering these results together with the CV profiles shown in Fig. 2d, it appears that the carbonyl/phenol redox reaction can occur on the surface of the MPC anode over the wide voltage range of $\sim 0.5$ to $\sim 1.9$ V.

Figure 2. Electrode properties of MPCs (with different O/C atomic ratios) and of a CB-coated MPC, at room temperature: (a) in situ CV profiles at a scan rate of 50 mV s$^{-1}$ and a scan number of 5 cycles, (b) impedance spectra, (c) electrical capacity as a function of O/C atomic ratio at a current density of 10 mA cm$^{-2}$, (d) in situ CV profiles for a CB-coated MPC at a scan rate of 10 mV s$^{-1}$ and a scan number of 5 cycles, (e) electrical capacity as a function of charge voltage at a current density of 10 mA cm$^{-2}$. The data provided in (a), (b) and (d) were obtained from uncoated or CB-coated MPC|SIPO-PTFE|Pt/C, air electrochemical cells while the remaining data were obtained from uncoated or CB-coated MPC|SIPO-PTFE|commercial RuO$_2$, air batteries.
Similar Raman band shifts have been reported for RuO$_2$ nanocrystals and thin films. It can also be seen from Fig. 3d that the intensity of the band at 630 cm$^{-1}$ was significantly lower in the case of the lab-made sample, possibly reflecting a difference in the microstructures or crystallite sizes of the two specimens.

The majority of studies using RuO$_2$ electrodes have been carried out in acid or alkaline solutions. In the present work, to better understand the characteristics of the present RuO$_2$ cathodes in atmospheric air, various in situ electrochemical measurements were conducted using the three- or two-electrode methods. CV profiles for the lab-made and commercial RuO$_2$ were recorded over the potential range of ±0.3 V (versus air reference), and a commercial Pt/C electrode was also assessed for comparison purposes. The three-electrode method generated ellipsoidal CV curves with a slope angle of approximately 45° relative to the x-axis (Fig. 4a). This is most likely due to the occurrence of faradaic reactions, in addition to a series of reversible redox transitions between various Ru oxidation states. In our previous study, analysis of the effluent gases from the RuO$_2$/C cathode showed that the H$_2$O concentration decreased and the O$_2$ concentration increased during charge and that the reverse occurred during discharge (faradaic efficiency ca. 60%). Given the similarity in the general shapes of the CV profiles obtained from the RuO$_2$ and Pt/C, it appears that oxygen reduction and oxygen evolution reactions (ORR and OER) occur during the cathodic and anodic scans, respectively, in parallel to the redox transitions between Ru$^{3+}$ and Ru$^{4+}$. Both the anodic and cathodic currents obtained from the lab-made RuO$_2$ at each potential were higher than those for the commercial RuO$_2$ and comparable to those generated by the Pt/C. The integrated area of the Pt/C device was greater, however, due to the large BET specific surface area (248 m$^2$ g$^{-1}$) of the carbon support. Importantly, the current from the Pt/C electrode continuously decreased as the scan number increased, while current outputs of the two RuO$_2$ electrodes remained almost unchanged after 100 scans. Carbon corrosion caused by the oxidation of carbon to CO$_2$ by water vapor is a well-known phenomenon in electrolysis and fuel cells, and can be summarized by the following reaction:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad [3]$$

The impedance spectrum of each of the three electrodes was skewed in the low frequency range of 0.1–20 Hz (Fig. 4b), due to the slow diffusion or adsorption of oxygen and/or water vapor. Both the skew angle and the degree of skew were the lowest in the case of the lab-made RuO$_2$. These variations in skew are possibly a result of the higher stability of RuO$_2$ compared to Pt/C in the acidic medium and of the difference in particle size between the two types of RuO$_2$. Based on its apparent superior properties, the lab-made RuO$_2$ was the focus of subsequent experiments.

The capacitive distribution in the CV profile remained symmetrical with respect to the potential of the reference electrode (Fig. 4a), indicating that the ORR and OER, as well as the reduction and oxidation reactions of Ru ions, had similar polarization resistance values. This same trend was also evident in the electrode potentials with IR correction during cathodic and anodic polarizations (Fig. 4c). We therefore conclude that the RuO$_2$ electrode exhibits high reversibility for both the faradaic and pseudo-faradaic reactions. This was further confirmed by the performances of fuel and electrolysis cells with the RuO$_2$ electrode. Specifically, an almost linear relationship between the current density and the cell voltage was maintained regardless of the polarity of the current sent through the cell (Fig. 4d).

**Characterization and electrochemical studies of electrolyte membranes.**—The electrolyte membrane used in our previous study was prepared by simply mixing SIPO powder with PTFE powder, followed by cold-rolling the mixture to a thickness of 250 μm. The resulting electrolyte had a density as high as 90 mg cm$^{-2}$. In the present study, a lighter electrolyte was obtained by employing a composite membrane composed of SIPO and sSEBS. It was found that the thickness of the SIPO-sSEBS composite membrane could be tailored from 36 to 137 μm. As an example, the SEM image of a 65 μm-thick composite membrane is shown in Fig. 5a, together with an image of

![Figure 3. Characterization of lab-made and commercial RuO$_2$: TEM images and SAED patterns for (a) lab-made and (b) commercial RuO$_2$, and (c) XRD patterns and (d) Raman spectra.](image-url)
Figure 4. Electrode properties of lab-made and commercial RuO$_2$ at room temperature: (a) in situ CVs at a scan rate of 50 mV s$^{-1}$ and a scan number of 5 cycles, (b) impedance spectra (for comparison, data for Pt/C are also included in (a) and (b)), (c) IR-corrected cathode potentials during anodic and cathodic polarizations as functions of current density (expressed as an absolute value) and (d) current density-voltage curves for fuel and electrolysis cells. All data were collected from H$_2$, Pt/C|SIPO-PTFE|lab-made or commercial RuO$_2$, air electrochemical cells.

a 250 $\mu$m-thick SIPO-PTFE composite membrane. More detailed information on the structure of this composite membrane was obtained by high magnification SEM, and a homogeneous dispersion of SIPO particles was seen throughout a cross-section of the membrane (Fig. S7). In addition, a relatively high density of SIPO was observed, with no visible pin-hole formation (Fig. 5b).

The proton conductivity of the SIPO–sSEBS composite membrane was compared with those of the individual materials and the SIPO-PTFE at various temperatures under non-humidified conditions (Fig. 5c). The proton conductivity of the SIPO-sSEBS composite membrane was lower than that of a SIPO pressed pellet, but much higher than that of a sSEBS polymer membrane. This was not unexpected because, like other sulfonated polymers, sSEBS ceases to function as a good proton conductor under dry conditions. Notably, the proton conductivity of the composite membrane was evidently increased by the use of sSEBS in place of PTFE at all the tested temperatures. This is because sSEBS is proton conductive, unlike PTFE. The sSEBS contains $-\text{SO}_3\text{H}$ groups available for proton transfer and therefore forms a proton-conducting pathway from one SIPO cluster to another.

To elucidate other physiochemical properties, hydrogen/air fuel cells were fabricated using SIPO-sSEBS composite membranes with various thicknesses as the electrolytes (Fig. 5d). Regardless of the temperature, slight decreases in the OCV were observed by reducing the thickness, attributed to crossover of hydrogen and/or oxygen molecules through the membrane. (The OCV observed at 85 $\mu$m was independent of temperature, likely due to the uncertainty in the measurements.) Moreover, the ohmic resistance of the composite membrane decreased almost linearly with decreasing thickness from 137 to 65 $\mu$m, below which the effect was insignificant. SEM images showing overhead (Fig. 5b) and cross-sectional views (Fig. S7) indicate the presence of a polymer-rich phase at the external surface of the composite membrane. Due to the lower proton conductivity of this phase, its formation would be expected to increase the ohmic resistance of the membrane, an effect that would become increasingly significant as the membrane thickness decreases. Thus, the optimal membrane thickness was determined to be 65 $\mu$m, a value that gave area-specific ohmic resistances between 0.5 and 0.8 $\Omega$ cm$^2$. OCVs between 0.90 and 0.95 V and a membrane density of 12 mg cm$^{-2}$.

Performance evaluation as an energy device.—A device was fabricated using a CB-coated MPC anode, a lab-made RuO$_2$ cathode and a SIPO-sSEBS electrolyte, and the resulting battery performance was evaluated. The device was charged and then discharged with a current density of 40 mA cm$^{-2}$ at various temperatures (Fig. 6a). At all the tested temperatures, the charge-discharge processes occurred with a coulombic efficiency of approximately 100% over the voltage range of 0.0–1.5 V. The charge voltage was reduced and the discharge voltage was enhanced by increasing the temperature, an effect that correlates with a decrease in the internal resistance of the cell at higher temperatures (Fig. S8). Consequently, the electrical capacity increased from 150 to 330 mAh g$^{-1}$ as the temperature was increased from ambient to 75°C. This can be explained by an increase in the accumulated anode potential, because both the resistive loss and overpotential during charge decrease with temperature and the charge voltage is the sum of the accumulated electrode potential, resistive loss and overpotential.

The effect of the current density on the charge-discharge properties of the device was investigated for current densities of 40–100 mA cm$^{-2}$ (Fig. 6b). Coulombic efficiencies over 95% were achieved in the tested current-density range. In addition, increased current density was found to lead to a decrease in the electrical capacity (Fig. S9) because the voltage rise/drop during charge/discharge also increased with the current density. An additional contributing factor may have been an...
Figure 5. Characterization and electrolyte properties of SIPO-sSEBS and PTFE composite membranes: (a) cross-sectional SEM images, (b) top-view SEM image and EDX elemental map for Sn in the SIPO-sSEBS composite membrane, (c) conductivities measured in non-humidified air (for comparison, data for a sSEBS membrane and a SIPO pressed pellet are also included) and (d) OCV and area-specific ohmic resistance as functions of membrane thickness for the H2, Pt/C|SIPO-sSEBS|Pt/C, air fuel cell.

Figure 6. Electrochemical performance of the CB-coated MPC|SIPO-sSEBS|lab-made RuO2 battery: (a) charge-discharge curves between room temperature and 75°C at a current density of 40 mA cm⁻², where the charge voltage was set at 1.5 V, (b) charge-discharge curves at various current densities and 75°C, where the charge voltage was set at 1.5 V, (c) capacity retention as a function of cycle number at 75°C, where the current density and charge voltage were set at 40 mA cm⁻² and 1.5 V, respectively, and (d) Ragone plot (for comparison, data for the battery used in the previous study are also included in (c) and (d)).
increase in the mass-transfer resistance of the anode with the current density, due to the restricted diffusion of ionicomers in the narrow micropores of the MPC. This is supported by the finding that the electrical capacity was almost independent of the quantity of MPC in the anode (Fig. S10), indicating a highly reversible charge-transfer reaction at the interface. Thus, the mass transfer in the micropores tends to be rate-determining in the higher current density range.

The cyclability of the device was evaluated with a current density of 40 mA cm$^{-2}$ at 75 °C (Fig. 6c). The electrical capacity remained unchanged after 300 cycles, in contrast to our previous result. The excellent cyclability of the present device is accomplished primarily through the use of the RuO$_2$ cathode instead of the RuO$_2$/C cathode, since this modification avoids corrosion of the carbon support. In addition, the formation of ruthenium tetroxide (RuO$_4$), which tends to degrade the cathode performance, may be suppressed at lower cathodic overpotentials during charging.

The performance of the present device was also compared with that of our previous device in terms of the energy and power densities normalized with respect to the total device weight (Fig. 6d). As a result of the improvement of each cell component, the present device provides energy densities of 26–47 Wh kg$^{-1}$ and power densities of 351–1114 W kg$^{-1}$, values that are approximately four times higher than those obtained from the previous unit. (The maximum volumetric energy and power densities of the present device were 52 Wh L$^{-1}$ and 758 W L$^{-1}$, respectively.) Notably, this performance is higher than those for redox-flow and lead-acid batteries, comparable to those for nickel-metal hydride batteries, but lower than those for lithium batteries.

Meanwhile, the discharge/charge efficiency of the present battery is as low as 55%, due to the relatively high internal resistance of the cell.

The present device also represents a type of fuel cell, although it does not require any fuel supply. Current density-voltage ($I$-$V$) curves were obtained by charging the device to 1.5 V at various temperatures, followed by discharge with a current-sweep rate set at 10 mA s$^{-1}$. The slope of the $I$-$V$ curves was reduced with increasing temperature (Fig. 7a), as expected based on the decreased internal resistance of the device (Fig. S8). Moreover, the slope of the $I$-$V$ curves was highly dependent on the quantity of MPC in the anode (Fig. 7b), as reflected by the increased hydrogen storage capacity of the anode. However, the short-circuit current density was not systematically proportional to the quantity of carbon, because all the high current-density sections do not reach a distinct limiting current.

The resulting peak power density was in the range of 105–214 mW cm$^{-2}$ (Fig. S11a)), values that are approximately one fifth of those obtained from conventional PEM fuel cells. To evaluate the fuel cell performance in more detail, the specific power and power density were normalized according to the total device weight and volume (Fig. S11b) and (c)). Both the specific power (5418–8727 W kg$^{-1}$) and power density (5.0–5.9 W cm$^{-3}$) were within the wide range of values reported for PEM fuel cells and higher than those of direct methanol fuel cells. It is noteworthy that there was a large difference in specific power values among the three cells, while the difference in power density was negligible. This distinction results from the large volume to mass ratio of the MPC; the MPC anode accounts for a relatively low proportion of the overall device mass, while comprising a large proportion of the total device volume.

Conclusions

A CB-coated MPC anode, a nanocrystalline RuO$_2$ cathode and a SIPO-sSEBS electrolyte membrane were prepared and characterized as cell components for RFCBs. The MPC anode was modified by acid treatment, followed by coating with a small quantity of CB. This modification increased the quantities of carbonyl and phenol groups on the MPC surfaces while maintaining low contact resistance between the MPC particles. The electrical capacity was found to be positively affected by increases in both the charge voltage and the temperature, due to the increased hydrogen storage capacity resulting from the carbonyl/phenol redox reactions. RuO$_2$ nanoparticles were obtained by the precipitation of metal chlorides from a neutral aqueous solution. This material had an amorphous-like nanostructure oriented in the direction of the (110) plane. It was determined that the ORR and OER both proceeded reversibly on the RuO$_2$ cathode at relatively low overpotentials. A homogeneous distribution of SIPO was achieved throughout a composite membrane composed of SIPO and sSEBS down to a membrane thickness of 65 μm without the formation of pin holes, and the density of the 65 μm-thick membrane was found to be 12 mg cm$^{-2}$. The resulting device exhibited battery characteristics with coulombic efficiencies over 95% when the current density and discharge-charge voltage were in the ranges of 40–100 mA cm$^{-2}$ and 0.0–1.5 V, respectively. An initial electrical capacity of 330 mAh g$^{-1}$ was found to be stable over 300 cycles. The maximum energy and power density values achieved with this device were 47 Wh kg$^{-1}$ and 1114 W kg$^{-1}$, respectively. The present device also functioned as a fuel cell with a peak specific power of 5418–8727 W kg$^{-1}$ and a peak power density in the range of 5.0–5.9 W cm$^{-3}$.

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Figure 7. Electrochemical performance of the CB-coated MPC|SIPO-sSEBS|lab-made RuO$_2$ fuel cell: current-density and voltage curves (a) for the cell between room temperature and 75 °C and (b) for the cell with various quantities of CB-coated MPC at 75 °C.
