Rechargeable PEM Fuel-Cell Batteries Using Porous Carbon Modified with Carbonyl Groups as Anode Materials

Kazuyo Kobayashi, Masahiro Nagao, Yuta Yamamoto, Pilwon Heo, and Takashi Hibino

Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8601, Japan
High Voltage Electron Microscope Laboratory, Ecotopia Science Institute, Nagoya University, Nagoya 464-8601, Japan
Fuel Cell Group, Samsung SDI Co. Ltd., Gyeonggi-do, 446-577, South Korea

Rechargeable fuel-cell batteries (RFCBs) operate by hydrogen storage and release at the anode, while oxygen evolution and reduction reactions occur at the cathode. High-surface-area porous carbon was treated with HNO3 to produce an anode material with carbonyl and phenol groups on the surface, thereby providing redox sites for hydrogen storage and release. The HNO3-activated carbon anodes were characterized with respect to use in a RFCB operated from room temperature to 75°C with a voltage range of 0–2.0 V. The quantity of carbonyl groups and the corresponding reduced phenol groups increased with the O/C atomic ratio of the oxidized carbon, by which the electrical capacity was increased to reach a maximum of 125 mAh g⁻¹ at an O/C atomic ratio of 0.114. The optimal temperature and charge voltage for performance and cyclability were determined to be 50°C and 1.25 V, respectively. The charge and discharge times remained at ca. 93% of the respective initial values after 300 cycles. The RFCB with the modified porous carbon anode provided 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).

Problems with energy supply and use are related not only to global warming, but also to environmental issues, and this has accelerated the development of highly efficient and environmentally-friendly power sources. In recent years, metal-air batteries have been the focus of significant interest in the field of advanced energy storage systems because they employ a lighter cathode that operates on abundant oxygen in the air. While these batteries offer the promise of very high energy densities, they only deliver current densities in the order of 1 mA cm⁻², which are one or two orders of magnitude lower than the required level. Safety and cyclability concerns must also be addressed for practical applications. In contrast, hydrogen-air fuel cells draw far higher current densities than those for metal-air batteries, while achieving energy densities comparable to those for metal-air batteries. Nevertheless, fuel must be continuously supplied from an external source; therefore, hydrogen production, storage, and distribution are required. To avoid the obstacles associated with these systems, rechargeable fuel cell systems, which operate with alternate electrolyzer and fuel cell modes, are considered an attractive and potentially viable power source. The key technology necessary for this application is hydrogen storage with high capacity and good cyclability. Currently, the standard hydrogen storage methods are cryo-adsorption on activated carbon, compressed gas tanks, and metal hydrides. However, hydrogen tanks require high pressures, while metal hydride systems release hydrogen at high temperatures, which would mean the fuel cell and the hydrogen storage systems would have to be separate.

As an alternative approach, a new concept of a unitized rechargeable fuel cell has been proposed by integration of a fuel cell with a hydrogen storage medium; however, such electrochemical systems should not be classified as fuel cells, because the fuel is not supplied from an external source, but is an integral part of the device. In addition, considering that the cathode potential is determined based on the equilibrium thermodynamic reaction, they should be distinguished from capacitors. Therefore, this type of device is designated as a rechargeable fuel cell battery (RFCB). Cyclohexane, methylcyclohexane, and decalin were at first regarded as promising hydrogen storage materials for RFCBs, but required high temperatures over 300°C for dehydrogenation of these hydrocarbons and over 250°C for dehydrogenation of the corresponding reduced hydrocarbons. In contrast, anthraquinone (AQ) had a large and stable redox potential at ca. −0.1 V (vs. Ag/AgCl), where AQ is hydrogenated to anthrahydroquinone (AH₂Q) during cathodic polarization and AH₂Q is dehydrogenated to AQ during anodic polarization. An RFCB based on the AQ/AH₂Q system demonstrated charge-discharge processes with coulombic efficiencies over 95% in the range 10–100 mA cm⁻². Moreover, stable cyclability was confirmed after 300 cycles from room temperature to 50°C, above which the electrical capacity became gradually lower as the cycle number increased. However, the obtained energy densities (0.8–3.4 Wh kg⁻¹), which were normalized according to the mass of the entire cell, were lower than those for other batteries, due to the low hydrogen storage capacities of AQ (0.9 wt%) and carbon (essentially 0 wt%).

The origin of the AQ/AH₂Q redox reaction is ascribed to the following equilibrium reaction between the carbonyl (C=O) and phenol (C-OH) groups.

\[
C=O + H^+ + e^- \leftrightarrow C-OH
\]

However, there are only two carbonyl groups in an AQ molecule. Moreover, AQ is an isolator compound, so that it must be supported on a carbon surface when used as an electrode, which further reduces the gravimetric hydrogen storage capacity of the entire electrode. It should also be noted that the AQ content in the electrode could not be increased to above 33 wt%, due to the formation of crystalline AQ particles. One promising method to overcome these limitations is to directly introduce a high density of carbonyl groups onto a high-surface-area carbon support, which would provide a number of redox sites for hydrogen storage and release on the anode surface.

Similar attempts have been made to develop pseudo-capacitive electrode materials for supercapacitors. Carbon nanotubes, graphene, and activated carbon can be functionalized using physical, chemical, and electrochemical processes. Among these, acid treatment is one of the most useful techniques to modify the carbon surface because there is less damage to the carbon structure. The goals of the present work were to (1) functionalize the anode material under various conditions, (2) characterize an optimized anode material, (3) conduct electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge-discharge, and cyclability tests from room temperature to 75°C, and (4) discuss the limitations of this RFCB and directions for future research.

*Electrochemical Society Active Member.
E-mail: hibino@urban.env.nagoya-u.ac.jp

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Experimental

Materials.— A Sn0.1In0.1P2O7 (SIPO) electrolyte membrane was synthesized according to a previously reported procedure.28 0.04 g of polytetrafluoroethylene (PTFE) powder was added to 1.0 g of SIPO powder, kneaded using a mortar and pestle, and then cold-rolled to a thickness of 250 μm using a laboratory rolling mill. The porous carbon (Maxsorbs MSC-30) used in this study was purchased from Kansai Coke and Chemicals. This carbon was modified by stirring 1 g of carbon in 50 ml of 6 or 24 wt% HNO3 at room temperature or 50 C for 29–111 h. After filtering and washing, the resultant anode products were dried in vacuum at 120 C for 6 h. A physical mixture of 50 wt% RuO2 (Aldrich) and 50 wt% carbon (Kansai Coke and Chemicals) was employed as a cathode material. The preparation procedure was the same as that described in our previous paper.15 The anode or cathode powder was dispersed with a small amount of H2PO4 ionomer39 (Wako Chemicals) using a mixer (Thinky AR-100) for 15 min. The obtained slurry was screen printed on the surface of a carbon fiber paper (Toray TGP-H-090). Unless otherwise stated, the anode and cathode loadings were adjusted to ca. 12 and 8 mg cm−2, respectively. For comparison, AQ/C (33 wt% AQ, 67 wt% Maxsorb) and Pt/C (40 wt% Pt, 60 wt% Vulcan) were also examined as anode and cathode materials, respectively.

Characterization.— The O/C atomic ratio of the samples was determined using energy-dispersive X-ray (EDX) spectroscopy installed in a scanning electron microscope (SEM; JEOL JSM-6610A) system. Transmission electron microscopy (TEM; JEOL EM-10000BU) and TEM-EDX elemental mapping were also conducted. The quantity of functional groups was measured according to the method suggested by Boehm.30 NaOH and NaHCO3 were used as reaction reagents for measurements of the total number of acidic groups (phenol and carboxyl (COOH) groups) and the number of carboxyl groups, respectively. For example, 0.05–1.0 g of sample was placed in a vessel, to which 50 ml of 0.004N NaOH was added. After stirring at 100 C for 2 h and filtering, the solution was back-titrated using 0.002N HCI. The number of phenol groups was assumed to be the difference between the NaOH and NaHCO3 consumed. Attenuated total reflection (ATR) infrared spectra were recorded using Fourier transform infrared (FT-IR) spectroscopy (Varian Varian-7000). The chemical charge states of C 1s and O 1s were analyzed using X-ray photoelectron spectroscopy (XPS; VG Escallab220i-XL). The pore characteristics of the samples were evaluated using nitrogen adsorption micro- and mesopore volume distributions were determined using the standard micropore method (MP) and the Barrett–Joyner–Halenda (BJH) method, respectively.11 The O2, H2O, and CO2 concentrations in the outlet gas from the electrolysis for charge and discharge were also determined using online gas chromatography (GC; Varian CP-2002).

Electrochemical measurements.— CV profiles for the anode were collected using a galvanostat/potentiostat (Hokuto Denko HZ-5000) in three-electrode mode, where the working electrode, an Ag/AgCl reference electrode, and a Pt counter electrode were set in a 0.5 M H2SO4 solution. Batteries were fabricated by sandwiching the electrolyte membrane between the two electrodes (0.5 cm2). The anode was attached to a stainless steel current collector and then sealed using thermal- and chemical-resistant PTFE tape (Nitto Denko). The cathode was supplied with atmospheric air at a relative humidity of ca. 50% and a flow rate of 30 ml min−1. The ohmic and polarization resistances were analyzed using an impedance analyzer (Solartron SI 1260) and an electrochemical interface (Solartron 1287) in the frequency range of 0.1–104 Hz with an AC amplitude of 10 mV. The electrical capacity was obtained from galvanostatic charge-discharge measurements with the current density and charge voltage set in the ranges of 10–100 mA cm−2 and 0.5–2.0 V, respectively. The voltage during charge and discharge was monitored using the impedance analyzer. Each electrode potential was separated by attaching a Pt/C reference electrode to the surface on the side of the electrolyte. The energy density was calculated by integrating the area under the voltage-time curve during discharge, which was then normalized according to the anode weight (ca. 6 mg) and with respect to the total cell weight (ca. 53 mg). The power density was also estimated by dividing the energy density by the discharge time.

Results and Discussion

Modification of carbon, part 1.— The carbon was treated with 6 wt% HNO3 at room temperature for 29 h to form carbonyl groups. As a result of this modification, an increase in the O/C atomic ratio from 0.010 to 0.055 was detected by SEM-EDX analysis. The O/C atomic ratio of 0.055 is close to that of 0.049 observed for the AQ/C sample. These results were further confirmed by TEM-EDX maps (Fig. 1), where the quantity of O for the carbon was homogeneously increased to almost the same level as that for the AQ/C sample.

The BET specific surface area of the carbon after HNO3 treatment (2163 m2 g−1) was somewhat lower than that before treatment (2433 m2 g−1) due to a decrease in the micro- and mesopores volumes (Fig. 2a).1.60 and 0.87 cm3 g−1 after HNO3 treatment, respectively. Thus, it is likely that surface oxides were produced in the micro- and mesopores of the carbon. The AQ/C sample possessed a smaller BET specific surface area of 1451 m2 g−1 due to its lower carbon content of 66 wt%. The total content of acidic groups in the carbon samples before and after HNO3 treatment was determined to be 0.097 and 0.464 Meq g−1, respectively, where phenol groups were the major acidic groups for both samples (Fig. 2b). Compared to the carbon after HNO3 treatment, the AQ/C sample had an approximately one-third less total content of acidic groups, which is not surprising, because neither NaOH nor NaHCO3 can react with carbonyl groups.29 (A portion of carbonyl groups in AQ could be converted into phenol groups, which were titrated with NaOH as shown in Fig. 2b.) The FT-IR spectrum for the carbon after HNO3 treatment indicated 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) (Fig. 2c). In contrast, the AQ/C sample had a sharp band at 1670 cm−1, which is assigned to carbonyl groups, although the reason for this shift to a lower wavenumber cannot be explained at present. Similar finding were obtained by XPS measurements, which revealed more intensive phenolic C–O (286.3 eV), carboxylic C–O (287.8 eV), and carboxylic COO (288.9 eV) peaks on the surface of the HNO3-activated carbons. Based on these results, it is concluded that carbonyl and the corresponding reduced phenol groups are successfully produced on the surfaces of the micro- and mesopores in the carbon by HNO3 treatment. Details of the role of carbonyl groups on the electrochemical properties will be discussed later.

Charge and discharge properties of RFBs with unmodified, modified, and AQ-containing carbon anodes.— CV profiles for the three electrodes revealed different curve shapes (Fig. 3a): the CV profile for the unmodified carbon was the most rectangular among them, while the CV profile for the modified carbon was heavily distorted from the rectangular shape, and the CV for the AQ/C showed large redox peaks at ED/2 = −0.15 V (vs. Ag/AgCl). The latter two phenomena are attributable to faradic reactions that occur on the surfaces of these electrodes according to Reaction 1; however, these reactions were much less potential-dependent for the modified carbon electrode than for the AQ/C electrode. Based on the literature, various types of carboxyl/phenoal groups are present on the surface of modified carbons,29 in contrast to only one type of carboxyl/phenoal group on the surface of the AQ/C system. It is also demonstrated that these functional groups are electrochemical active in the wide potential window of 0–1 V. Therefore, such redox reactions appear as a broad band or wave rather a peak in the CV curve, unlike that for AQ. Alternatively, as noted by Jelet et al., redox peaks cannot be observed at fast scan rates when the reaction proceeds quasi-reversibly. Therefore, the modified carbon may present slower kinetics for the redox reaction than the AQ/C system. The CV profiles also showed that
Figure 1. TEM images (upper panel) and TEM-EDX elemental maps for O (lower panels) on the (a) unmodified carbon, (b) modified carbon, and (c) AQ/C samples.

while the integrated area for the modified carbon was approximately 2 times higher than that for the unmodified carbon, the integrated area of the AQ/C electrode was somewhat decreased due to its small BET specific surface area. It should be noted that the ratio of the integrated area between the unmodified and modified carbons is not in agreement with their total quantity of carboxyl and phenol groups. This discrepancy can be explained by assuming that the formation of an electrical double layer (EDL) accompanies the redox reaction, which would reduce the contribution of the redox current density to the total current density.

Figure 2. Characterization of unmodified, modified, and AQ-containing carbons. (a) BET specific surface areas and the micropore (MP) and mesopore (BJH) volumes. (b) Acidic functional group contents. (c) FT-IR spectra. (d) XPS spectra.
Figure 3. Electrochemical performance of batteries at room temperature. (a) CV profiles at a scan rate of 50 mV s$^{-1}$ and a scan number of 5 cycles. (b) Voltage changes of the batteries charged to 1.0 V at a current density of 10 mA cm$^{-2}$, followed by circuit opening. (c) Galvanostatic charge-discharge curves for the batteries at a current density of 10 mA cm$^{-2}$. (d) Galvanostatic discharge curves for the batteries with different electrode weights at a current density of 10 mA cm$^{-2}$.

To determine whether the carbonyl/phenol redox reaction occurs in a cell with the SIPO-PTFE electrolyte, this cell was charged to 1.0 V and the circuit was then opened at room temperature (Fig. 3b). As a result of the charge, plateaus appeared at 0.85 V for the modified carbon anode, at 0.80 V for the AQ/C anode, and at 0.79 V for the unmodified carbon anode. Considering that the OCV obtained with the AQ/C anode is close to that expected from the $E_{1/2}$ value and that an almost equivalent OCV was generated from the cell with the Pt/C cathode, this OCV is ascribed to the potential difference between the carbonyl/phenol redox reaction shown by Reaction 1 and the oxygen reduction reaction (ORR) shown in Eq. 2.

$$2H^+ + 2e^- + 1/2O_2 \leftrightarrow H_2O \quad [2]$$

The validity of Reaction 2 was confirmed by analyzing the outlet gas from the RuO$_2$/C cathode. Although the accuracy of this analysis is not high, especially for H$_2$O, because the measurement was conducted at a low current density of 10 mA cm$^{-2}$, the H$_2$O concentration decreased and the O$_2$ concentration increased during charge, and vice versa during discharge (Supplementary Information, Fig. S1). However, the anode potentials of the other two cells should be attributed not only to the redox potential, but also to the EDL potential; therefore, they may be defined as pseudo-capacitive potentials. In any event, the production of hydrogen molecules is avoided because the charge voltage of 1.0 V is far below the critical voltage necessary for the hydrogen reduction reaction and the oxygen evolution reaction (OER).

Galvanostatic charge-discharge profiles for the cells with the three anodes were measured with a current density of 10 mA cm$^{-2}$ at room temperature (Fig. 3c). For all the tested cells, the charge-discharge processes occurred with a coulombic efficiency of approximately 100%. More importantly, the charge/discharge time for the cell with the modified carbon anode was extended up to that for the cell with the AQ/C anode, which is due to an increase in the redox capacitance for this anode. (The EDL capacitance of the modified carbon anode may be smaller than that of the unmodified carbon anode due to its smaller BET specific surface area.) No voltage plateau was observed during charge and discharge (Fig. 3c), because a high current density of 10 mA cm$^{-2}$ was applied to the cell with a large internal resistance of 2.6 $\Omega$ cm$^{-2}$ at room temperature. However, this battery did exhibit a plateau-like discharge voltage above 0.8 V for over 500 s when operated at a low current density of 0.5 mA cm$^{-2}$ (Supplementary Information, Fig. S2).

It is necessary to determine which component is responsible for the electrical capacity of the present device. Therefore, the dependency of the discharge time on the amount of anode and cathode was evaluated under the same conditions (Fig. 3d). The discharge time was prolonged from 209 to 678 s when using three times the amount of anode, but was almost independent of the amount of cathode. Therefore, the electrical capacity of the cell is confirmed to be dependent on the hydrogen storage capacity of the modified carbon anode. This can easily be understood by monitoring each electrode potential with respect to the Pt/C reference electrode exposed to ambient air. The changes in the potential of the modified carbon anode during charge and discharge were more significant than those of the RuO$_2$/C cathode (Supplementary Information, Fig. S3). Further evidence is provided by the retention of an almost equivalent discharge time (ca. 180 s) when using a Pt/C cathode instead of a RuO$_2$/C cathode (Supplementary Information, Fig. S4).

Modification of carbon, part 2.— To further enhance the density of carbonyl groups on the carbon surface, the HNO$_3$ treatment was conducted under various conditions. The EDX spectral intensity due to O for the modified carbon gradually increased with the treatment time, the HNO$_3$ concentration, and the temperature (Fig. 4a). More importantly, the charge/discharge time for the cell with the modified carbon anode was extended up to that for the cell with the AQ/C anode, which is due to an increase in the redox capacitance for this anode. (The EDL capacitance of the modified carbon anode may be smaller than that of the unmodified carbon anode due to its smaller BET specific surface area.) No voltage plateau was observed during charge and discharge (Fig. 4b), because a high current density of 10 mA cm$^{-2}$ was applied to the cell with a large internal resistance of 2.6 $\Omega$ cm$^{-2}$ at room temperature. However, this battery did exhibit a plateau-like discharge voltage above 0.8 V for over 500 s when operated at a low current density of 0.5 mA cm$^{-2}$ (Supplementary Information, Fig. S2).
area of the carbon decreased almost linearly with the O/C atomic ratio (Supplementary Information, Fig. S5); however, the carbon with an O/C atomic ratio of 0.131 maintained relatively large micropore (1.08 cm$^3$ g$^{-1}$) and mesopore (0.55 cm$^3$ g$^{-1}$) volumes. This implies that the carbon surface is partially oxygenated without significant structural deformation. This oxygenation led to an increase in the number of acidic groups on the carbon surface from 0.097 to 2.560 mEq g$^{-1}$ (Fig. 4b). A good relationship between the total number of acidic groups and the O/C atomic ratio was established, except when the O/C atomic ratio was 0.131. One possible explanation for this exception is that the proportion of carbonyl groups, which are not quantified by the titration method employed, is lower for the carbon with an O/C atomic ratio of 0.131, compared to those for the other carbons. It is possible that a number of carbonyl groups may be oxidized to carboxyl groups in this sample, due to the severe acid treatment.

More detailed information on the functional groups introduced is provided by FT-IR and XPS characterization of the HNO$_3$-treated carbons. In the FT-IR spectra, the intensities of the C–OH (3000–3600 cm$^{-1}$), C=O (1720 cm$^{-1}$), and COO$^-$ (1580 cm$^{-1}$) bands increased with O/C atomic ratio (Fig. 4c). There was an abrupt increase in the intensity of the C=O stretching band (1190 cm$^{-1}$) of the carboxyl group at O/C atomic ratios of 0.114 and 0.131. FT-IR observations also showed that while the intensity of carboxylic COO$^-$ band (288.9 eV) increased with the O/C atomic ratio, the intensity of carboxylic C=O band (287.8 eV) reached a plateau at an O/C atomic ratio of 0.114 (Fig. 4d, Supplementary Information, Fig. S6). Another important result is that the O/C atomic ratios calculated from the XPS data were 10–45% higher than those calculated from the EDX data, the extent of which was more significant at O/C atomic ratios of 0.114 and 0.131. This suggests that the carbon is more oxygenated on the external surface than on the internal surface, especially under severe acid treatment conditions.

Charge and discharge properties of RFCBs with modified carbon anodes: effect of O/C atomic ratio.— The capacitive characteristics of the carbons with different O/C atomic ratios were measured at room temperature. The CV profiles showed three distinctive changes with O/C atomic ratio; both the anodic and cathodic currents increased at each potential, the shape varied from rectangular to oval or ellipsoidal, and the slope angle increased to 45$^\circ$ or higher relative to the x-axis (Fig. 5a). Only the carbon with an O/C atomic ratio of 0.131 deviated from these patterns, which will be discussed together with the electrochemical properties of carboxyl groups later.

Fig. 5b shows typical characteristics for the cells with the modified carbon anodes charged and then discharged at a current density of 10 mA cm$^{-2}$. At each time, the charge voltage was reduced and the discharge voltage was enhanced by an increase of the O/C atomic ratio, with the exception of the carbon with an O/C ratio of 0.131. Consequently, the electrical capacity increased with the O/C atomic ratio, reaching a maximum of 125 mAh g$^{-1}$ at an O/C atomic ratio of 0.114, and then decreased (Fig. 5c). The observed high capacity is considered to be related to an enhanced carbonyl/phenol redox reaction, which is attributed to an increase in the total number of these groups, as is evident from the approximately linear relationship between the capacity and O/C atomic ratio in Fig. 5c. It is also reasonable to consider that the effect of the EDL on the charge-discharge properties becomes smaller as the O/C atomic ratio increases, due at least to the associated decrease of the BET specific surface area.

The internal resistances of the cells with the modified carbon anodes were compared using room temperature impedance
Figure 5. Electrochemical performance of batteries using modified carbon anodes with different O/C atomic ratios at room temperature. (a) CV profiles at a scan rate of 50 mV s\(^{-1}\) and a scan number of 5 cycles. (b) Galvanostatic charge-discharge curves for the batteries at a current density of 10 mA cm\(^{-2}\). (c) Electrical capacity as a function of the O/C atomic ratio at a current density of 10 mA cm\(^{-2}\). (d) Impedance spectra for the batteries.

measurements (Fig. 5d). The intercept of the impedance line and the real axis, which corresponds to the ohmic resistance, was almost constant at 1.6 \(\Omega\) cm\(^2\) in the range of O/C atomic ratio from 0.055 to 0.097; however, it increased to 2.7 and 3.8 \(\Omega\) cm\(^2\) at O/C atomic ratios of 0.114 and 0.131, respectively. Similar increases in the depressed arc in the middle frequency range (15 Hz–100 kHz) were observed, which is associated with the charge-transfer resistance, and in the skewed line in the low frequency range (0.1–15 Hz), which is due to the slow diffusion of oxygen and/or water vapor. Thus, this poor electrode performance is the most likely cause of the decrease in electrical capacity observed at an O/C atomic ratio of 0.131. As discussed in the following section, the anode potential applied by charging the cell, which determines the redox capacitance, is reduced by both the resistive loss and overpotential of the cell, which results in a decrease of electrical capacity. (The cell with the carbon anode with an O/C atomic ratio of 0.114 had the highest electrical capacity, as a result of the trade-off between resistance and capacitance.)

The electrical conductivity of carbon generally decreases with surface oxygen concentration.\(^{42,43}\) Although there are no reports that correlate the conductivity with the concentration of certain functional groups, it is speculated that the carboxyl group is one of the least conductive functional groups, which explains the poor electrical contact between the carbon particles with an O/C atomic ratio of 0.131. Moreover, the carboxyl group has little reversible redox ability at low temperatures,\(^{44}\) therefore, the oxygenation of carbon without the formation of such functional groups is a beneficial approach in terms of electrode design for RFCBs. Subsequent experiments were conducted using the carbon anode with an O/C atomic ratio of 0.097, which possesses both low electrical resistance and high redox capacitance.

Charge and discharge properties of RFCBs under various conditions.—The cell was charged with current densities of 10–100 mA cm\(^{-2}\) at room temperature and the OCVs were measured under open-circuit conditions for 700 s (Fig. 6a). The self-discharge current was recorded to be a few microamps in all trials, whereas the OCV was significantly reduced by an increase in the current density. The applied voltage is the sum of the accumulated electrode potential, resistive loss, and overpotential. The latter two values become larger as the current density increases; therefore, the OCV, which is the difference between the electrode potentials, is reduced with increasing current density by compensation. The electrical capacity was also negatively affected by the current density (Fig. 6b), as reflected by the decrease in the OCV. An additional contributing factor may be an increase in the mass-transfer resistance of the anode with current density, due to the restricted diffusion of ionomer ions in the narrow micropores of the carbon.

The influence of the charge voltage on the OCV was also investigated with a current density of 10 mA cm\(^{-2}\) at room temperature (Fig. 6c). The OCV increased at higher charge voltages ranging from 0.50 to 1.75 V. In the CV profile of the anode (Fig. 5a), this electrode does not have fixed redox potentials, which allows a broad OCV window, depending on the charge voltage. However, the cell exhibited a rapid increase in voltage from ca. 1.7 to 2.0 V during charging, followed by a large decrease from 2.0 V to an OCV of ca. 1.4 V (Fig. 6c), which is comparable to the OCV when charged to 1.75 V. These phenomena indicate that the hydrogen production reaction proceeds during charge at over 1.7 V; the produced hydrogen escapes from the anode through an aperture in the sealing tape. In addition, the electrolyte employed possesses a limited withstanding voltage because there is the possibility of electrochemical reduction of the constituent Sn\(^{4+}\) and In\(^{3+}\) ions to their respective low-valent ions, which could cause an electrical short-circuit of the cell during charge. Thus, charge voltages greater than 1.5 V are not suitable for stable operation of this RFCB. A positive charge-voltage dependency of the electrical capacity was obtained (Fig. 6d), which is opposite to its negative current-density dependency. In particular, a high electrical capacity of 268 mAh g\(^{-1}\)
was achieved in the voltage range of 0–1.5 V. It should be noted that the observed capacity is not proportional to the charge voltage, but is relatively greater, which cannot be explained by a simple model of EDL capacitors that sustain a certain constant current against the potential in the CV profiles.

Our previous study demonstrated that the redox reaction between AQ and AH₂Q molecules was promoted by operation of the cell at elevated temperatures. To assess whether a similar effect could occur for the carbonyl and phenol groups on the modified carbon anode, galvanostatic charge-discharge profiles of the present device were measured with a current density of 10 mA cm⁻² at various temperatures. The OCV increased slightly with the operation temperature (Fig. 7d). This is correlated to a decrease in the internal resistance of the cell with the temperature (Fig. 7d), which reduces both the resistive loss and overpotential, so that the accumulated anode potential is enhanced. Moreover, the charge/discharge time increased significantly with the operation temperature (Fig. 7b), which is also due to a decrease in the internal resistance of the cell. As a result, the electrical capacity reached 202 mAh g⁻¹ at 75 °C (Fig. 7c).

AC impedance spectra revealed three important features (Fig. 7d). Firstly, the ohmic resistance was strongly dependent on the operation temperature, which reflects the large proton conductivity dependence of the electrolyte on the temperature. Secondly, the charge-transfer resistance was reduced by an increase in the temperature, which is ascribed to the enhanced kinetics of both the redox reaction at the anode and the ORR/OER at the cathode at elevated temperatures. Thirdly, the sharp rise in the low frequency range was not parallel to the imaginary axis, which indicates that these electrodes do not function as simple EDL electrodes. Moreover, the decrease in the degree of this rise with the temperature is due to an acceleration of proton diffusion in the narrow micropores at the anode, which enhances surface utilization for the redox reaction. Accordingly, such enhanced diffusion contributes to an increase in electrical capacity, which is also responsible for the inflection of the charge curve around 0.8 V at 50°C (Fig. 7b).

Cyclic charge-discharge characteristics.— To evaluate the cyclability of the present device, galvanostatic charge-discharge measurements were performed under various conditions. In all trials, coulombic efficiencies greater than 95% were obtained for the charge-discharge cycles, even if the cell was seriously degraded during 300 cycles (see for instance Fig. 8a), where the operation temperature, current density, and charge voltage were set at 75°C, 40 mA cm⁻², and 1 V, respectively. The effects of current density, charge voltage, and operation temperature on the cyclability are summarized as follows: 1) the cyclability was insensitive to the current density, although the capacity was slightly reduced at a low current density of 10 mA cm⁻² (Fig. 8b); 2) the cyclability was significantly affected by the charge voltage, the extent of which increased with the charge voltage (Fig. 8c); 3) the cyclability was lower only at 75°C, below which the capacity remained unchanged (Fig. 8d). A common cause of the lowered cyclability is degradation of the cathode, because the capacity recovered to approximately 100% of each initial value by replacement of the cathode in the test cells (see the last data points in Figs. 8b, 8c and 8d). As reported previously, this cathode degradation could be attributed to corrosion of the carbon support during charging:

\[ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \]  \[ (3) \]

The production of HO₂ - radical intermediates as active oxygen species was confirmed by in situ Raman analysis during OER, by which the carbon would be oxidized to carbon dioxide. Moreover, evidence for Reaction 3 is provided by the excellent cyclability of the cell with a cathode consisting of only RuO₂, even after 300 cycles at 75°C (Supplementary Information, Fig. S7), although the capacity...
Figure 7. Influence of operation temperature on the electrochemical performance for a battery with a modified carbon anode (O/C atomic ratio = 0.097). (a) Voltage changes of the battery charged to 1.0 V at various temperatures, followed by circuit opening. (b) Galvanostatic charge-discharge curves for the battery between room temperature and 75 °C at a current density of 10 mA cm$^{-2}$. (c) Electrical capacity as a function of operation temperature, where the current density and the charge voltage were set at 10 mA cm$^{-2}$ and 1 V, respectively. (d) Impedance spectra for the battery between room temperature and 75 °C.

Figure 8. Cyclability of battery with modified carbon anode (O/C atomic ratio = 0.097) under various conditions. (a) Galvanostatic charge-discharge curves for the battery between the 1$^{st}$ and 300$^{th}$ cycles, where the operation temperature, current density, and charge voltage were set at 75 °C, 40 mA cm$^{-2}$, and 1 V, respectively. (b) Capacity retention as a function of cycle number at various current densities, where the operation temperature and the charge voltage were set at room temperature and 1 V, respectively. (c) Capacity retention as a function of cycle number at various charge voltages, where the operation temperature and the current density were set at room temperature and 40 mA cm$^{-2}$, respectively. (d) Capacity retention as a function of cycle number at various temperatures, where the current density and the charge voltage were set at 10 mA cm$^{-2}$ and 1 V, respectively.
was somewhat reduced due to an increase in the ohmic resistance of the cathode.

**Evaluation as an energy storage device.**—From these results, it is expected that the optimal balance of performance and cyclability would be obtained at an operation temperature of 50 °C and a charge voltage of 1.25 V. The cell was thus charged and then discharged under such conditions. The charge and discharge times remained at ca. 93% of the respective initial values after 300 cycles. (Supplementary Information, Fig. S8). A comparison between the modified carbon and AQ/C anodes was conducted with respect to the energy and power densities, which were normalized with respect to the anode weight. The modified carbon provided higher energy densities than those normalized not only according to the AQ/C weight, but also according to only the AQ weight under the same conditions, where the temperature and charge voltage were 75 °C and 1 V, respectively (Fig. 9a). It should be noted that the theoretical O/C atomic ratio of AQ molecules is 0.286, which is much higher than that of 0.097 for the carbon anode. This could be because AQ is not highly dispersed in the molecular form; very weak diffraction peaks assigned to AQ were observed in an X-ray diffraction (XRD) pattern of the AQ/C sample (Supplementary Information, Fig. S9). Therefore, it is demonstrated that the carbonyl groups introduced into the carbon function more effectively as hydrogen storage media than the carbonyl groups in AQ deposited on a carbon surface. Moreover, the energy density could be further enhanced by operation of the cell under optimal conditions with the temperature and charge voltage at 50 °C and 1.25 V, respectively (Fig. 9a). This implies that the charge voltage is a more significant contributing factor to the energy storage capacity of the cell than the operation temperature. The performance of the present device was also compared with that for other energy storage devices in terms of the energy and power densities normalized with respect to the total cell weight. The energy densities (2.5–13.8 Wh kg⁻¹) and power densities (46.4–296.3 W kg⁻¹) were comparable with those for lead-acid batteries, but lower than those for nickel-metal hydride batteries (Fig. 9b). The present device may also be regarded as a proton exchange membrane fuel cell. Therefore, current-voltage and current-power density curves were measured under almost standard fuel-cell conditions with the charge voltage and temperature at 1 V and 75 °C, respectively. The resulting peak power densities were strongly dependent on the current-sweep rate: 102, 87, 73, and 64 mW cm⁻² at 20, 10, 5, and 3 mA s⁻¹, respectively (Supplementary Information, Fig. S10). This dependency is due to the limited hydrogen storage capacity of the anode.

Further research is required to enhance the performance of the present device. The electrolyte encompasses approximately 70–80% of the total cell weight; therefore, fabrication of a thinner electrolyte membrane is a necessary requirement to realize lightweight devices. The fabrication of inorganic-organic composites is a promising method to produce such membranes. The carbon modification process should also be optimized to effectively increase the density of carbonyl groups on the carbon surface while maintaining good electrical contact between the carbon particles. Moreover, alternative non-carbon supports are required for the development of cathodes that would enable operation of the cell at higher charge voltages. Another challenge for the present device is low charge/discharge efficiencies. For example, under the optimized conditions stated, the efficiency was 81% at 10 mA cm⁻², but 39% at 60 mA cm⁻². The decrease in the charge/discharge efficiency is due to the voltage rise and drop during charge and discharge, respectively, which is attributed to the relatively large internal resistance of the cell. However, this problem is mostly overcome with thinner electrolyte films and by establishing better electrical contact between the carbon particles.

**Conclusions**

A porous carbon was treated to increase the quantity of carbonyl and phenol groups on the surface. TEM-EDX and N₂ adsorption measurements revealed that surface oxides were produced in the micro- and mesopores of the modified carbon. An OCV of ca. 0.8 V was generated in a cell with the modified carbon electrode by charging to 1.0 V, and charge-discharge proceeded with a coulombic efficiency of approximately 100%, which is attributed to the redox capacitance based on the reaction between carbonyl and phenol groups. The electrical capacity was highest for an O/C atomic ratio of about 0.1, which was consistent with the CV and AC impedance data. The charge and discharge characteristics of the cell with the optimized anode were evaluated under various conditions. The electrical capacity was negatively dependent on the current density due to a decrease in the OCV with increasing current density, but was positively affected by the charge voltage, which was improved by an increase in both the OCV and capacitance with the charge voltage. Operation of the cell at elevated temperatures reduced its internal resistance, and increased its electrical capacity. The cyclability was reduced at a charge voltage of 1.5 V and at a temperature of 75 °C, where corrosion of the carbon support was severe during charging. The optimal temperature and charge voltage for the cell were 50 °C and 1.25 V, respectively. The resulting RFCB functioned as a secondary battery with an energy density of 2.5–13.8 Wh kg⁻¹ and a power density of 46.4–296.3 W kg⁻¹.

**References**

1. M. Winter and R. J. Brodd, *Chem. Rev.*, 104, 4245 (2004).
2. S. E. J. Flipsen, *J. Power Sources*, 162, 927 (2006).
