Electrical and Physical Properties of Carbonized Charcoals

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Because coal does not conduct electricity and graphite is costly and inert, little attention has been given to the development of a carbon fuel cell (i.e., a battery that utilizes a consumable carbon anode to generate electrical power). In this work we show that a packed bed of carbonized charcoal particles subject to a compressive pressure (ca. 8 MPa) can be a good electrical conductor ($\sigma < 0.2 \ \Omega \cdot \text{cm}$). Low electrical resistivities $\sigma$ are manifest by many different charcoals after carbonization at a heat treatment temperature (HTT) of 950 °C. The 5 orders of magnitude decrease in the electrical resistivity of charcoal with increasing HTT from 650 to 1050 °C is not associated with any dramatic change in the carbons’ X-ray diffraction spectrum, its Fourier transform infrared spectrum, or its elemental analysis. Our findings cause us to visualize carbonized charcoal to be a macromolecular, cross-linked, three-dimensional, aromatic structure replete with conjugation and $\pi$ bonds that facilitate the movement of electrons, as well as nanopores, and micromolecular cracks. Because charcoal powder is competitive in price with fossil fuels and because carbonized charcoal is extremely reactive with a volumetric energy density (in a compacted packed bed) comparable to conventional liquid fuels, compact packed beds of carbonized charcoal hold promise for use as electrodes and consumable anodes in fuel cells. The packed-bed apparatus we describe is a prototype anode for use in a biocarbon fuel cell.

Introduction

Carbon batteries played an important role in the history of fuel cell research. Sixteen years after Grove1 demonstrated an “electrolyte gas cell” that gave an open-circuit EMF of about 1 V between H$_2$ and O$_2$, Becquerel attempted to build a fuel cell that consumed coal.2,3 Unfortunately, the electrolyte contained a nitrate that attacked the carbon without producing a current. Later Jablonski2,3 tested an apparatus modeled on a similar concept. By the end of the 19th century, the increasing demand for electric power began to consume considerable amounts of coal because the conversion efficiency was low (3%).1 Contemplating this problem, in 1894 Ostwald1 called for development of a fuel cell that would react carbon with oxygen to produce electricity more efficiently than thermomechanical equipment. Two years later in Boston J acques13 demonstrated a 1.5-kW battery that employed a consumable carbon anode, an iron cathode, and an air-bubbled alkali hydroxide electrolyte to generate 0.9 V at 400–500 °C. Operating intermittently, this battery delivered power with an overall efficiency of 32% during a 6-month period. The experiment failed because carbonates accumulated in the electrolyte that halted the electrochemistry.1 In 1904 Haber and Bruner1 showed that the Jacques anode actually involved the production of hydrogen as an intermediate in the electrochemistry. However, Haber was unable to build a practical carbon fuel cell. In 1937 Baur and Preis3 tested a fuel cell that used a coke anode and an electrolyte composed of zirconia stabilized with magnesia or yttria at $>1000{^\circ}\text{C}$. Vielstich explains that the high temperature was needed because of the low reactivity of the carbon fuel.1 No practical carbon fuel cells resulted from the work of Baur and Preis.

Interest in carbon fuel cells resurfaced during the 1970s, when the Stanford Research Institute (SRI) attempted to develop a coal-based fuel cell that employed molten lead at temperatures of 500–900 °C.4,5 This work was abandoned in 1981. Recently, Scientific Applications and Research Associates6 reported progress in further developing the SRI concept. At Stanford University, Gur and Huggins7 demonstrated a high-temperature (725–955 °C) fuel cell that employed stabilized zirconia as a solid electrolyte and a graphite anode. To the best of our knowledge, these recent developments have not led to the demonstration of a practical carbon fuel cell. Summarizing the status of carbon fuel cells, Bockris and Srinivasan8 concluded that carbon fuel cells are impractical because (i) coal is not an electrical conductor and (ii) graphite is too scarce and expensive to be used as a fuel. Thus, the history of carbon fuel cell research suggests that the chief obstacles to the development of a biocarbon fuel cell are...
the electrical conductivity of the biocarbon, its cost, and its reactivity.

It has been known for centuries that biocarbons can possess very high electrical conductivities. In 1810 carbonized charcoal electrodes were used in an arc lamp, and in 1830 carbonized charcoal was used as an electrode for primary batteries. These electrodes were made from powdered charcoal or coke bonded with sugar syrup or coal tar, pressed, and carbonized. Recently, Coutinho, Luengo, and their co-workers reported extensive studies of biocarbon electrodes manufactured from charcoal particles bonded together by wood tar and subsequently carbonized. The measured electrical resistivity of the electrode fell to $10^{-2}$ $\Omega \cdot cm$ for carbonization at temperatures above 900 °C. This background suggests that carbonized charcoal could be used to fabricate the consumable anode of a carbon battery. Furthermore, we remark that charcoal can be produced from biomass inexpensively in yields that approach the theoretical limit. Carbonized charcoal is also easy to store, and an established infrastructure exists to deliver charcoal to consumers worldwide. Moreover, carbonized charcoal, unlike graphite, is extremely reactive. For these reasons we have a keen interest in the development of biocarbon fuel cells. The first step is to establish baseline data for the electrical properties of carbonized charcoal electrodes. In this paper we present data that describe the effects of increasing carbonization temperature on the properties of carbonized charcoal particles, including their electrical resistivity in a packed bed subject to compressive force, their chemical and physical composition as determined by elemental analysis, Fourier transform infrared (FTIR), and X-ray diffraction (XRD) spectra, and their surface area. We focus on a carbonization temperature of 950 °C because earlier work has proven the high reactivity of this biocarbon. The packed-bed apparatus employed in this work is now being used as the anode of a biocarbon fuel cell, whose performance will be the subject of future papers.

**Apparatus and Experimental Procedures**

The raw biomass materials that served as substrates to produce the high-yield charcoals employed in this study were obtained as representative grab samples in Hawaii. The high-yield and flash carbonization charcoals were produced according to procedures described in earlier publications.

**Carbonization Procedures.** A tubular furnace (Applied Test Systems 3210) with temperature control (Applied Test Systems XT-16), which can reach temperatures as high as 1200 °C, was employed to carbonize the high-yield charcoal samples. A quartz tube (122 cm length and 1.99 cm i.d.) was placed within the furnace and used to carbonize a measured amount of charcoal in a ceramic boat. By location of type K thermocouples in the boat, it was possible to accurately measure the heat treatment temperature (HTT) of the charcoal. UHP nitrogen gas was delivered at 1.0 L/min to the tube during the carbonization process, thereby ensuring that the carbonization process, including the heat-up and cool-down steps, occurred in an inert environment. In a few cases, charcoals were carbonized within a closed crucible in a muffle furnace (Barnstead Thermolyne FB1215M). This procedure was employed in our earlier work and is able to carbonize larger quantities of charcoal more conveniently than the tubular furnace.

Unfortunately, several weaknesses accompany the use of a muffe furnace. First (and perhaps foremost), the muffle furnace thermocouple (TC) reports its own temperature, which is neither the temperature of the furnace nor the temperature of the carbon within the closed crucible. Our studies indicate that the muffle furnace TC reports a temperature about 30–40 °C higher than the temperature of the outer surface of the ceramic crucible. The measurement of the carbon temperature within the closed crucible is not easy; consequently, we do not know how large of a temperature gradient exists between the outer surface of the crucible and the center of the carbon bed in the closed crucible. Second, the lid of the crucible leaks a little air; consequently, the carbonization is not accomplished in a truly inert environment.

**FTIR Analyses.** The FTIR spectra were measured by a FTIR spectrometer system (Perkin-Elmer 1710), including a DTGS (deuterated triglycerine sulfate) detector, DRIFT accessory, and microsampling. The specimens were examined in powder form, using KBr as the reference material. The spectra were recorded from 4400 to 400 cm$^{-1}$ by averaging 100 scans at 4-cm$^{-1}$ resolution.

**XRD Analyses.** XRD measurements were carried out for phase and crystal structure identification with a Philips PW1710 diffractometer using Cu K$_\alpha$ radiation and a graphite monochromator (45 kV, 35 mA, and divergence 1°). Average crystallite size ($L_{ave}$) and deformation (lattice strain, $\varepsilon$) were determined from single-line profile Fourier (Voigt method) analysis.

**Brunauer–Emmett–Teller (BET) Surface Area and Total Pore-Volume Analyses.** An automatic gas sorption analyzer (Quantachrome Aurosorb-1) was used to determine the specific surface area and total pore volume of the carbonized charcoals. After a vacuum outgas step at 483 K for 4 h, the nitrogen-adsorption isotherm was measured at liquid-nitrogen temperature (77 K). The BET method was employed to determine the surface area from a limited linear region of the adsorption isotherm, usually 0.05 < $P/P_0$ < 0.35. The total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure close to unity ($P/P_0$ > 0.99). To validate our surface area determinations, we measured the surface area of a commercial Barnebey and Sudcliffe (B&S) coconut shell activated carbon (AC). Our result (1201 m$^2$/g) was close to the value reported by B&S (1106 m$^2$/g) for bulk samples.

**Electrical Resistivity.** The electrical resistivity of the biocarbon samples was determined by a two-probe packed-bed technique at room temperature (ca. 20 °C). As shown in Figure 1, the nickel electrodes at the top and bottom of the 1.9-cm-diameter packed bed, contained in an alumina tube, enable measurement of the electrical resistance of the bed. The packed bed is compressed by the upper electrode, which is forced against the bed by a pneumatic piston. Note that the electrodes are insulated from the apparatus by Teflon and alumina. The electrical resistance of the packed bed is measured with a precision, hand-held milliohmmeter (ISOTK M210). This meter has a resolution of 0.001 $\Omega$ from 0 to 1.990 $\Omega$, a resolution of 0.01 $\Omega$ from 1.99 to 19.90 $\Omega$, and a resolution of 0.1 $\Omega$ from 19.9 to 199.9 $\Omega$. Our setup mimics the apparatus originally employed by Mrozowski in his pioneering work but was designed to enable its future use as the anode of a carbon fuel cell. The resistivity, $\rho$, in ohm centimeters, is given by the equation $\rho = RA/l$, where $R$, $A$, and $l$ are the...
measured resistance in ohms, cross-sectional area of the bed in square centimeters, and length between the probes in centimeters, respectively. Note that the measured length (i.e., the offset of the piston in Figure 1 relative to its empty bed position) is not the exact length \( l \) of the bed because of the compression of the nickel electrode and the stretching of the stainless steel threaded rods that results from the compressive force applied to the packed bed. To account for these effects, we measured the change in the apparent length of an empty bed (i.e., zero offset length) over the range of applied pressures used in this work (see Figure 2). After an initial small, nonlinear change in length (due to slack in the system), the change in the zero offset length was linear with pressure. The Hook's law slope of the line \((-3.23 \times 10^{-3} \text{ cm/MPa})\) displayed in Figure 2 is nearly identical with the theoretical value \((-3.34 \times 10^{-3} \text{ cm/MPa})\) calculated using Young's moduli of Ni 200 and SUS 316 and the appropriate geometric factors for the elements of the cell under compression and tension. We used the Hook's law formula to correct the zero offset value of the instrument, and this correction resulted in a decrease in the calculated values of the packed bed's resistivity and its bulk density. Higher compressive pressures and shorter bed lengths had a bigger impact on this correction. In the case of a compressive pressure of 9.5 MPa and a bed length of 0.1 cm, the correction resulted in a ca. 35\% decrease of the measured resistivity and the apparent bulk density of the packed bed.

Finally, we remark that we easily detected the Seebeck voltage (created by temperature differences between the two biocarbon–nickel interfaces\(^{24–26}\)) when the ceramic tube, containing compressed carbonized charcoal, was heated to temperatures above 29 °C. As expected, no thermoelectric effect was observed when the apparatus was unheated and in thermal equilibrium at room temperature.

**Results**

Unless noted otherwise, the carbons listed in Table 1 were prepared in the tubular furnace at the indicated HTT with a soak time of 10 min. Typically two to three boat lots were needed to produce enough carbonized charcoal for subsequent analyses. As expected, the mass loss of the macadamia nut shell (machshell) charcoal increased monotonically with increasing HTT, except for the 1050 °C sample that was produced from a sample of flash carbonization charcoal with a much lower volatile matter content. The elemental analyses of these carbons showed a scattered progression from 87.9 to 95.13 wt % carbon with increasing HTT accompanied by concomitant decreases in the H and O contents of the samples. The high ash content of the 850 °C carbon must represent inhomogeneities present in the charcoal samples. Recall that the 1050 °C carbon was derived from a different machshell charcoal sample than the other carbons, and this might explain its high nitrogen content. Values of the H/C and O/C ratios of the machshell carbons (see Table 2) decreased monotonically, except for the 950 °C sample. Of the remaining carbons listed in Tables 1 and 2, the Leucaena wood carbon resembles the Kukui nut shell carbon (except for their respective ash contents). A comparison of the 950 °C carbons reveals a considerable range in the values of each of the properties listed in Tables 1 and 2.

**FTIR Analyses.** The FTIR spectra of the machshell carbons prepared at 650–850 °C are displayed in Figure 3. For comparison, the spectrum of the machshell charcoal substrate and that of a Sigma–Aldrich synthetic graphite are also indicated. Note that all spectra are displayed on a linear absorbance scale and each curve is drawn one unit higher than the one beneath it. This approach facilitates the comparison of the relative intensities of the spectra. Weak features at about 2350 cm\(^{-1}\) belong to CO\(_2\) absorption of air. H\(_2\)O adsorbed on the KBr reference material gives weak, broad, inverse bands at about 3400 and 1630 cm\(^{-1}\) in the spectra of
Table 1. Carbonized Charcoals Employed in This Work

<table>
<thead>
<tr>
<th>feed</th>
<th>HTT, °C</th>
<th>burnoff, %</th>
<th>surface area, m²/g</th>
<th>pore volume, ml/g</th>
<th>elemental analysis, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>macshell</td>
<td>650</td>
<td>21</td>
<td>216</td>
<td>0.135</td>
<td>C: 87.90, H: 2.19, O: 6.69, N: 1.04, S: 0.05, Ash: 1.17</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>22</td>
<td>169</td>
<td>0.115</td>
<td>C: 90.71, H: 1.63, O: 5.97, N: 0.95, Ash: 1.12</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>30</td>
<td>194</td>
<td>0.132</td>
<td>C: 90.03, H: 0.89, O: 5.66, Ash: 1.00, N: 0.06, S: 4.51</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>32</td>
<td>244</td>
<td>0.164</td>
<td>C: 89.98, H: 0.90, O: 6.04, N: 1.11, Ash: 1.61</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>22</td>
<td>NA</td>
<td>0.193</td>
<td>C: 95.13, H: 0.37, O: 2.82, N: 1.43, Ash: 1.07</td>
</tr>
<tr>
<td>Kukui nut shell</td>
<td>950</td>
<td>NA</td>
<td>22</td>
<td>NA</td>
<td>C: 92.92, H: 0.54, O: 4.52, N: 1.26, Ash: &lt;0.05, S: 1.49</td>
</tr>
<tr>
<td>coconut husk</td>
<td>950</td>
<td>NA</td>
<td>437</td>
<td>NA</td>
<td>C: 85.08, H: 0.72, O: 8.39, N: 0.91, S: 0.05, Ash: 5.63</td>
</tr>
<tr>
<td>Leucaena wood</td>
<td>950</td>
<td>NA</td>
<td>310</td>
<td>NA</td>
<td>C: 92.15, H: 0.46, O: 3.99, N: 1.15, Ash: 0.05, S: 2.45</td>
</tr>
</tbody>
</table>

Table 2. H/C and O/C Ratios for the Carbonized Charcoals Employed in This Work

<table>
<thead>
<tr>
<th>feed</th>
<th>HTT, °C</th>
<th>H/C</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>macshell</td>
<td>650</td>
<td>0.2969</td>
<td>0.0571</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.2141</td>
<td>0.0494</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>0.1178</td>
<td>0.0472</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>0.1192</td>
<td>0.0504</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>0.0463</td>
<td>0.0223</td>
</tr>
<tr>
<td>Kukui nut shell</td>
<td>950</td>
<td>0.0693</td>
<td>0.0365</td>
</tr>
<tr>
<td>coconut husk</td>
<td>950</td>
<td>0.1008</td>
<td>0.0740</td>
</tr>
<tr>
<td>Leucaena wood</td>
<td>950</td>
<td>0.0595</td>
<td>0.0325</td>
</tr>
</tbody>
</table>

Figure 3. Effect of HTT on the FTIR spectra of macshell char. The spectrum of the synthetic graphite is shown for comparison. (Each curve is drawn one unit higher than the curve beneath it.)

Figure 4. Absorbance spectra of carbonized charcoals compared with a synthetic graphite sample (750 °C). The characteristic bands found in the synthetic specimen are shown (OH, CH, CO, aromatic). Untreated macshell charcoal.
ized at increasing temperatures. Unexpectedly, the XRD spectra undergo almost no visible change with increasing HTT above 750 °C. Table 3 demonstrates this observation. The scattering domains of the macshell carbons contain only two or three layers in the 002 direction. Small increases in both $L_{002}$ and $\epsilon$ indicate some increase of ordering as a function of HTT in the macshell experiments. The estimated aromaticity $\gamma_a$ of the domains does not significantly increase with HTT above 750 °C. Figure 7 displays the XRD spectra of the 950 °C carbonized charcoals. These spectra are similar, except for the presence of small peaks that arise from the presence of inorganic species (mineral impurities) in the carbon. The broad, featureless peaks displayed in Figure 7 bear little resemblance to the broad peak at $2\theta = 25^\circ$ associated with the XRD spectra of a turbostratic carbon (Monarch 71) displayed in Figure 5 of Walker and Seeley,38 the heat-treated coals and petroleum coke displayed in Figure 4 of Senneca et al.,39 or the sharp peaks associated with heat-treated Australian black coals reported by Lu et al.37 As indicated in Table 3, the scattering domain of these carbons contains only two or three layers in the 002 direction. The size of these domains is significantly smaller than those (six or seven layers) reported by Kercher and Nagle40 for various hardwood and softwood medium-density fiberboard charcoals. Values of $\epsilon$ for these carbons exceed that of the 750 °C macshell carbon. The estimated aromaticity $\gamma_a$ of these carbons is high (much higher than those reported by Lu et al.37 for Australian black coals) but significantly lower than that of graphite.

### Surface Area and Pore-Volume Distributions

Table 1 displays the BET surface areas and (in some
the total pore volumes of the carbonized charcoal samples discussed above. Although the carbonization technique employed in this study was not designed to enhance the porous structure of the substrate, some of the biocarbon samples evidenced surprisingly high BET surface areas (e.g., 437 m²/g). Earlier workers reported values between 100 and 200 m²/g for macshell charcoal carbonized at 900–950 °C. In the case of the macshell carbon, the lack of a clear trend in the development of surface area with increasing HTT may reflect gross heterogeneities in the surface properties of the macshell charcoal. Both macshells and Kukui nut shells are rich in oil that forms a coke during pyrolysis. This coke must have a low surface area. It is possible that the scatter in the macshell data and the very low surface area of the Kukui shell carbon are a result of coked nut oils. More generally, we remark that 50 years ago Franklin called attention to the existence of “a large volume of extremely small holes” within highly porous, nongraphitizing carbons (e.g., sugar charcoal). The presence of extremely narrow pores in the biocarbons listed in Table 1 complicates the determination of their surface areas and pore volume distributions. In an earlier paper, we presented scanning electron microscopy photographs of macshell charcoals, but these do not display the nanoporous structures that are responsible for the high surface areas of these carbons.

**Electrical Resistivity.** Because few studies have been reported of the electrical properties of packed beds of biocarbons, we initiated this work with measurements of a commercially available B&S coconut shell AC and a commercial graphite powder that serve as reference materials. The B&S AC is attractive because it can be sieved to a useful particle size (20–40 mesh) and it is quite homogeneous. The graphite powder is a logical reference material, but its very fine particle size makes it difficult to handle.

Figure 8a displays the resistivity and bed length as a function of applied compressive pressure for a 0.506-g packed bed of 20–40-mesh AC. After an initial compression of the bed, the influence of the compressive pressure on the measured resistivity and length of the bed and its apparent bulk density are reproducible with little hysteresis. Although Mrózowski observed creep in his measurements of packed-bed resistivity, we detected no significant, systematic creep over a 60-min period. In Figure 8a, the resistivity of the bed decreases to a value of 0.41 Ω·cm at a bulk density of 0.61 g/mL under a compressive pressure of 7.63 MPa. Note that, after the initial compaction, the packed bed is virtually incompressible. Parts b and c of Figure 8 display identical behavior for packed beds of 1.0 and 1.5 g (respectively). Figure 8d confirms the expected ohmic behavior of the packed bed under a compressive pressure of 7.6 MPa. The slope of the solid, least-squares line (filled symbols) yields a resistivity of 0.44 Ω·cm. This value is in good agreement with the individual single-point values. Data points (open symbols) along the dashed line represent values of the measured resistance offset by the measured empty-cell resistance. This empty-cell resistance included the contact resistance between the two Ni electrodes as well as the resistance of the two Ni electrodes, etc. The measured empty-cell resistance was largely independent of the applied pressure. All of our reported values of resistivity were corrected by subtraction of the measured empty-cell resistance from the measured total resistance at the pressure of interest. The y intercept of the solid line (8 mΩ) in Figure 8d represents the sum of the empty-cell resistance and the contact resistances between the two Ni electrodes and the carbon bed. The y intercept of the dashed line represents the difference between the empty-cell Ni−Ni contact resistance and the two Ni−C contact resistances. This difference approximates the error incurred when we correct for the Ni−C contact resistance by use of the Ni−Ni (empty-cell) contact resistance. As displayed in Figure 8d, this error is small (<1 mΩ) relative to the resistance values of the packed bed (>40 mΩ). Related data for a smaller particle size (<105 μm) are displayed in Figure 8e. In this case the AC reaches a bulk density of 0.81 g/mL (see Table 4) with a resistivity of 0.26 Ω·cm under a compressive pressure of 11.5 MPa. At 7.86 MPa, the measured resistivity (0.35 Ω·cm) of the <105-μm powder (with a bed density of 0.78 g/mL) is somewhat less than the value (0.41 Ω·cm) associated with the 20–40-mesh material (with a bed density of 0.61 g/mL) under a compressive pressure of 7.63 MPa. This comparison suggests that the electrical resistivity of the packed bed is not strongly dependent upon either the particle size or the apparent bulk density of the bed (see below).

Figure 9 displays similar data for a 2.00-g packed bed of 1–2-μm graphite powder. The very fine particle size combined with the lubricity of the graphite powder causes the bed to be unusually compressible. Under a compressive pressure of 7.77 MPa, it evidenced a resistivity of 0.029 Ω·cm at a bulk density of 1.41 g/mL. We remark that the compressive pressure caused the packed bed of graphite particles to become a wafer that retained its integrity when removed from the apparatus, although the wafer was easily broken by hand. By way of comparison, the density of solid graphite is 2.26 g/mL, and the electrical resistivity of single crystals of graphite is anisotropic, with values as low as 40 μΩ·cm in the a−b plane at 300 K.

We have no knowledge of the conditions that were employed to produce the commercial AC used to acquire the data displayed in Figure 8. In particular, we have no knowledge of the carbon's HTT, i.e., its peak temperature. To put a floor on this value, we carbonized...
the AC in the muffle furnace at 950 °C and measured its resistivity as a function of compressive pressure. The values displayed in Figure 10 follow trends similar to those of Figure 8 but with a resistivity of 0.25 Ω·cm and a bulk density of 0.60 g/mL under a compressive pressure of 7.61 MPa. The carbonization treatment had little effect on the packed-bed density, but it lowered the resistivity by 43%. Evidently, the commercial activation treatment did not involve a peak temperature above 950 °C.

Ostensibly, this result appears to contradict the claim of some earlier workers\textsuperscript{44-46} that increasing the porosity of a carbon decreases both its thermal and its electrical conductivities. We remark that oxygen chemisorption can increase the electrical resistivity of a carbon;\textsuperscript{47} hence, the relatively low electrical conductivity of the AC may reflect its aggressive chemisorption of oxygen from the air.

As shown in Figure 12, a packed bed of the 20–40-mesh macshell carbonized charcoal (950 °C) evidences an electrical resistivity of 0.12 Ω·cm at a bulk density of only 0.45 g/mL. Despite its low density, the coconut husk carbonized charcoal is a better conductor of electricity than the commercial coconut shell AC.
of 0.53 g/mL under a compressive pressure of 7.97 MPa. To learn more about the effects of HTT on the electrical resistivity of carbonized charcoals, we also carbonized macshell charcoal at HTT of 1050, 850, 750, and 650 °C. Figure 12 displays the effect of increasing compressive pressure on the resistivity of each of these carbons, which decreases by more than 5 orders of magnitude with an increase of HTT from 650 to 1050 °C. As displayed in Figure 12, the 1050 °C macshell carbon's resistivity is about twice that of the graphite powder. Because these values approach the limit of detectability of our equipment, the exact ratio may differ somewhat from a factor of 2. Under a compressive pressure of 7.8 MPa, the apparent bulk density of the packed bed decreases from 0.71 to 0.58 g/mL as the HTT increases.

<table>
<thead>
<tr>
<th>Feed</th>
<th>HTT, °C</th>
<th>Particle size, a mesh</th>
<th>Sample weight, g</th>
<th>Resistivity, b Ω-cm</th>
<th>Density, b g/cm³</th>
<th>Energy content, c MJ/kg</th>
<th>Energy density, c GJ/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>macshell</td>
<td>650</td>
<td>20–40</td>
<td>0.24</td>
<td>6.6 × 10¹</td>
<td>0.70</td>
<td>35.0</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>20–40</td>
<td>0.37</td>
<td>2.9 × 10¹</td>
<td>0.65</td>
<td>35.0</td>
<td>22.8</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>20–40</td>
<td>0.45</td>
<td>5.8 × 10⁻¹</td>
<td>0.65</td>
<td>33.8</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>20–40</td>
<td>0.50</td>
<td>1.1 × 10⁻¹</td>
<td>0.58</td>
<td>34.9</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>20–40</td>
<td>0.51</td>
<td>5.9 × 10⁻²</td>
<td>0.61</td>
<td>35.1</td>
<td>21.4</td>
</tr>
<tr>
<td>Kukui nut shell</td>
<td>950</td>
<td>20–40</td>
<td>0.50</td>
<td>1.8 × 10⁻¹</td>
<td>0.82</td>
<td>34.9</td>
<td>28.6</td>
</tr>
<tr>
<td>coconut husk</td>
<td>950</td>
<td>20–40</td>
<td>0.49</td>
<td>1.8 × 10⁻¹</td>
<td>0.46</td>
<td>33.4</td>
<td>15.4</td>
</tr>
<tr>
<td>Leucaena wood</td>
<td>950</td>
<td>&lt;105 µm</td>
<td>0.50</td>
<td>1.6 × 10⁻¹</td>
<td>0.44</td>
<td>34.6</td>
<td>15.2</td>
</tr>
<tr>
<td>AC d</td>
<td>20–40</td>
<td>0.51</td>
<td>4.2 × 10⁻¹</td>
<td>0.63</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20–40</td>
<td>1.00</td>
<td>4.3 × 10⁻¹</td>
<td>0.62</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20–40</td>
<td>1.50</td>
<td>4.3 × 10⁻¹</td>
<td>0.64</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>carbonized AC d</td>
<td>950</td>
<td>&lt;105 µm</td>
<td>0.50</td>
<td>3.3 × 10⁻¹</td>
<td>0.81</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>graphite powder</td>
<td>1–2 µm</td>
<td>2.00</td>
<td>2.3 × 10⁻¹</td>
<td>0.63</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>

a U.S. standard sieve size or particle size before the heat treatment. b Resistivity and density values upon the second depressurization. c Estimated using the correlation of Cordero et al. (see text). d AC = activated carbon.
from 650 to 950 °C. This decrease is due to increased porosity of the carbon at higher HTT.

The 20-40-mesh Kukui shell carbon (see Figure 13) evidences a electrical resistivity (0.18 Ω·cm) similar to those of the coconut husk and macshell carbons but at a bulk density of 0.82 g/mL. The apparent bulk density (0.44 g/mL) of the 20-40-mesh Leucaena wood carbonized charcoal at 7.61 MPa (see Figure 14) is less than the macshell and Kukui shell carbons; nevertheless, its electrical resistivity (0.16 Ω·cm) is almost the same. To gain further insight into this matter, we carbonized Leucaena charcoal powder (<105 μm) and measured its resistivity. As displayed in Figure 14a, the powder evidences a slightly lower resistivity at the highest compressive pressures employed. On the other hand, the bulk density of the packed bed of powder (0.78 g/mL in Figure 14b) is nearly double that of the 20-40-mesh particles. Taken together, these findings indicate that the porosity of a carbonized charcoal does not significantly influence the electrical conductivity of the carbon.

For comparison sake, Espinola et al. reported a resistivity of 1.24 Ω·cm for a packed bed of Babacu nut carbon at 19.6 MPa and 0.272 Ω·cm at 98 MPa. Likewise, they reported a resistivity of 0.92 Ω·cm for Euclayptus lignin carbon at 19.6 MPa and 0.19 Ω·cm at 98 MPa. Unfortunately, Espinola et al. did not indicate the HTT of their carbons; consequently, this comparison is not very meaningful.

**Discussion**

The transformation of biomass into charcoal involves the loss of 60% or more of the substrate's mass with the evolution of nearly 4 mol of gas/mol of "monomer". During this transformation, the pyranose ring framework of the cellulosic fibers that compose biomass is grossly rearranged to form aromatic structures. Because this transformation does not involve a liquid phase, the product carbonaceous solid is inherently porous at the molecular level. Franklin elucidated some aspects of this transformation in her classic XRD study of crystallite growth in graphitizing and nongraphitizing carbons. She found that oxygen-rich substances (e.g., sugar) form nongraphitizing carbons that have relatively low densities and are microporous, very hard, and composed of a randomly oriented, cross-linked structure of graphitelike crystallites. The nanoporous structure combined with the random orientation of the crystallites prevents graphitization, even at HTT as high as 3000 °C. Nevertheless, we remark that Franklin employed a sugar charcoal produced via a 2-h heat treatment at 1000 °C prior to carbonization at 2160 °C and higher, whereas we observe graphitelike electrical resistivities following carbonization at 950-1050 °C for only 10 min. Surprisingly mild conditions impart graphitelike electrical properties to nongraphitizing carbons.

In a series of papers, Mrozowski and coworkers showed that the electrical resistivity of a packed bed of coke particles (subject to HTT of 1200 °C or more) decreased with increasing pressure (to the −0.5 power) and also decreased with increasing particle size (to the −0.25 power). No limit to the conductivity was reached at pressures as high as 100 MPa. The dependence of resistivity on pressure evidenced hysteresis and changed with increasing time at constant pressure (i.e., "creep"). On the other hand, we observed no creep and little hysteresis after an initial compaction of the bed. Furthermore, we found that neither the compressive pressure applied to the packed bed, the size and porosity of the particles composing the bed, nor the porosity of the bed had a big impact on its electrical resistivity under a compressive pressure of 5-10 MPa. We believe that some of these differences can be explained by a crushing of the bed at the high pressures...
employed by Mrozowski. Our equipment would not accommodate such high compressive pressures. Furthermore, such pressures are not needed to obtain a workable anode in a fuel cell. Moreover, the stability of the packed bed (as in our work) would be a desirable property of an electrode employed in a fuel cell.

There are similarities between the 9 orders of magnitude decrease in the electrical resistivity of compacted packed beds of fossil coke subject to increasing HTT as high as 1100 °C reported by Mrozowski and the macshell biocarbon resistivities listed in Table 4. On the other hand, Pinnick showed that a plot of log $\sigma$ vs (HTT)$^{-1}$ for a typical coke fell along a perfectly straight line, whereas such a plot of our data does not fall on a straight line. Some of the differences between our findings and those of Mrozowski may be due to the fact that all of the carbons employed in his work became liquid when heated and remained liquid up to 450 °C. As mentioned earlier, there is no liquid-phase precursor to charcoal. It is well-known that charcoal retains the form and structure of its biomass precursor to such an extent that the appearance of a charcoal can be used to identify its origin.

The plot of log $\sigma$ vs the H/C ratio displayed by Waters for fossil carbons resembles the data displayed in Tables 2 and 4. Waters also observed a plateau in electrical resistivity for atomic ratios H/C < 0.1. On the other hand, the value of O/C reported by Waters was a factor of 5–10 smaller than the values obtained in this work.

The 950 °C carbonized charcoals tested in this work spanned a large range of carbon contents, ash contents, H/C and O/C ratios, surface areas, porosities, particle sizes, and packed-bed densities. Nevertheless, at a given HTT, their FTIR spectra, XRD spectra, and electrical resistivities were quite similar to each other. Furthermore, at HTT ≥ 950 °C, their FTIR spectra and their electrical resistivities were similar to those of graphite particles. On the other hand, the XRD spectra of macshell charcoal underwent virtually no change at increasing HTT from 750 to 950 °C. Evidently, the 3 orders of magnitude decrease in electrical resistivity (with increasing HTT from 750 to 950 °C) is not associated with any change in the crystal structure of the biocarbon. Furthermore, the biocarbon XRD spectra do not resemble those of graphite or turbostratic carbons. These facts cause us to visualize carbonized charcoal to be a macromolecular, cross-linked, three-dimensional, aromatic structure replete with conjugation and $\pi$ bonds that facilitate the conduction of electrons, as well as nanopores, and micromolecular cracks. The evolution of about four molecules of gas per molecule of biomass “monomer” during carbonization leaves behind many dangling bonds (unpaired electrons) that may also contribute to the electrical conductivity of the carbon. Nevertheless, Shafizadeh and co-workers showed that the concentration of unpaired electrons (“free radicals”) in cellulose char peaked at HTT between 500 and 600 °C and thereafter declined by a factor of 5 at a HTT of 800 °C. Consequently, there is no evident relationship between the concentration of unpaired electrons in biocarbons and their electrical resistivity. The fossil carbon literature also contains speculations about the potential effects of mineral impurities on the electrical resistivity of the carbon. These impurities may act as donors or acceptors and thereby improve the electrical conductivity of the carbon semiconductor. It is evident that biocarbons also contain mineral impurities that could influence their electrical conductivity. Nevertheless, if we recognize that these biocarbons were produced from greatly different biomass substrates that must represent different ash compositions, it would be a case of real serendipity if they all contained an influential impurity that imparted to each carbon a similar electrical conductivity.

If we employ the correlation proposed by Cordero et al. for the higher heating value (HHV) of charcoal (i.e., HHV/MJ = 0.3543 (% fC) + 0.1708 (% VM), where % fC and % VM are the percentage fixed carbon and volatile matter contents of the charcoal, respectively), and assume that the 950 °C charcoals contain only ash and fixed carbon, then the energy content of these carbons is about 35 MJ/kg (see Table 4). This value is somewhat lower than those of liquified natural gas (LNG; ca. 55 MJ/kg), propane (ca. 50 MJ/kg), and crude oil (ca. 44 MJ/kg) but much higher than those of most coals. Table 4 also displays the energy density of these carbons on a volumetric basis. These values range from 15.2 to 28.6 GJ/m$^3$ and can be compared to the energy density of gasoline (i.e., octane with a lower heating value of 32 GJ/m$^3$), ethanol (ca. 21 GJ/m$^3$), LNG (23 GJ/m$^3$), and propane (24 GJ/m$^3$). When it is recognized that these carbon packed beds retain their bulk density after an initial compaction, it is evident that dense carbon packed beds are attractive energy carriers with energy densities comparable to those of conventional liquid fuels.

**Conclusions**

1. After an initial compaction, a packed bed of carbonized charcoal particles is virtually incompressible and evidences ohmic behavior under a compressive pressure of 7.6 MPa. The contact resistance between the bed and the two electrodes is negligible at this pressure. We observed no creep, little hysteresis, and little effect of pressure (between 5 and 10 MPa) on the resistivities of packed beds of carbonized charcoals after the initial compaction.

2. Surprisingly mild conditions (HTT ≈ 950 °C) impart graphitelike electrical properties to all of the charcoals that we studied.

3. The electrical resistivity of a packed bed of carbonized charcoal is not strongly dependent upon the particle size of the bed material, the surface area or the microporosity of the bed material, or the apparent bulk density of the packed bed.

4. The energy content of carbonized charcoal (ca. 35 MJ/kg) is somewhat lower that of than crude oil but higher than those of most coals. The energy density of a compact bed of carbonized charcoal (15.2–28.6 GJ/m$^3$) is comparable to that of conventional liquid fuels (e.g., propane, LNG, and ethanol).

5. Some carbonized charcoals have surprisingly high BET surface areas (e.g., 437 m$^2$/g), whereas others have negligible surface area. The presence of extremely narrow pores in carbonized charcoals complicates the determination of their surface areas and pore-volume distributions.

6. Increasing the HTTs between 750 and 950 °C has no significant effect on the XRD spectra of macshell charcoals. A wide range of charcoals carbonized at 950 °C manifest nearly identical XRD spectra. The scatter-
ing domains of graphite crystallites in the carbonized charcoals are less than three layers thick.  

7. All biocarbons obtained from macshells, Leucaena, coconut husk, and Kukui nut shell charcoals with HTT of 950 °C show FTIR spectra very similar to each other, as well as to the spectrum of graphite.

8. A comparison of the 950 °C biocarbons reveals a considerable range in the values of their C, H, O, and ash contents and the H/C and O/C ratios. None of these values is closely associated with the electrical conductivity of the biocarbon.

9. The transformation of biomass into biocarbon involves the loss of 60% or more of the substrate's mass with the evolution of nearly 4 mol of gas/mol of “monomer” of biomass. During this transformation, the pyrolysis of the cellulose fibers that decompose to a carbonaceous solid that is highly reactive and nose ring framework of the cellulose fibers that compose the biocarbon.

10. In light of the facts that (a) under compressive pressure a compact packed bed of carbonized charcoal can have an electrical resistivity comparable to that of a compact packed bed of graphite particles, (b) a compact carbonized charcoal packed bed can have a very large surface area and high reactivity as well as an energy density comparable to that of conventional liquid fuels, and (c) the wholesale price of biomass charcoal is competitive with gasoline and natural gas, we conclude that compact packed beds of carbonized charcoal have promising applications as electrodes and consumable anodes in biocarbon fuel cells and batteries. To explore these applications further, we are currently testing a biocarbon fuel cell that employs the packed bed apparatus described herein as its anode. Results of this work will be the subject of future papers.

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