The closed topology and tubular structure of carbon nanotubes[1–3] make them unique among different carbon forms and provide pathways for chemical studies. A number of investigations[4–8] have been carried out to find applications of nanotubes in catalysis, hydrogen storage, intercalation, etc. Since carbon-electrode-based fuel cells have been experimented with for decades, it is of importance to learn the electrocatalytic performance of these new carbon structures. We report here results of the electrocatalytic reduction of dissolved oxygen (important H2–O2 fuel cell reaction), using microelectrodes constructed from multiwalled nanotubes. In parallel, ab initio calculations were performed for oxygen deposited on the lattice and defect sites[9] of nanotube surfaces to determine the charge transfer during oxygen reduction and compared with similar reactions on planar graphite.

The microelectrodes were constructed in the following way (see Fig. 1). Multiwalled nanotubes (10 mg) prepared by the electric arc discharge process[9] and liquid paraffin (4 µL) were intimately mixed, placed in the narrow cylindrical slot of a Perspex holder and then packed by smooth vibration. The assembly was cured at 50 °C for 30 min. From the inner side of the Perspex, contact to a copper lead was made through conducting paint. Carbon paste electrodes (based on commercially available graphite powder) were prepared similarly. Carbon nanotube electrodes were prepared earlier by similar techniques to probe biocatalytic reactions.[9]

The need for oxygen reduction at catalytic surfaces has been recognized in fuel cells, batteries, and many other
electrodes applications.[10–16] Hence, oxygen reduction at nanotube surfaces is of great interest. Electrochemical reduction of dissolved oxygen is carried out in aqueous acidic (H2SO4) and neutral media (1 M KNO3). The solution is first degassed by bubbling nitrogen gas for about 15–30 min in order to record the background current–voltage curves. Under these conditions, no cyclic voltammetric peak in the potential range 0 to –0.8 V were observed. The same solutions were then saturated with oxygen by bubbling oxygen gas for 15 min. The cyclic voltammetric curve showed a well-defined peak at Epc = –0.31 V vs. SCE (saturated calomel electrode) in H2SO4 solution (pH 2) at the carbon nanotube electrodes. At the carbon paste electrodes only an ill-defined peak is seen at Epc = –0.48 V. In the KNO3 medium (pH 6.2), the reduction of dissolved oxygen is observed at Epc = –0.51 V at the carbon nanotube electrode. This peak is shifted at the carbon paste electrode by about 30 mV. The shift of the peaks, corresponding to the reaction on the nanotube electrodes, is a strong indication of the electrocatalysis on this electrode (see discussion below). The shift may be considered as an overpotential, which indicates a more facile reaction occurring at the nanotubes compared to other carbons. The electrochemical reduction of oxygen is a function of pH of the medium[10,11] as proton participation occurs as described by Equation 1.

\[ \text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \]  

This reaction has been well discussed in literature.[10] The reduction potential of oxygen will shift the pH of the solution due to Reaction 1. The reduction at a metal cathode proceeds through its dissociative adsorption. The peroxide formation is a consequence of the differences in the rate of electron transfer and in the rate of oxygen dissociation to adsorbed oxygen atoms. Peroxide can then be formed as a suitable intermediate. Oxygen therefore undergoes a 2e\(^{-}\) reduction. However, if the oxygen reduction proceeds through a superoxide ion and a subsequent protonation, as
[O₂ + e⁻ \rightarrow O₂⁻; O₂⁻ + HA \rightarrow HO₂ + A⁻] \tag{2}

The reduction potential of HO₂ + e⁻ \rightarrow HO₂⁻ is estimated as \(-0.74\) from the free energy data. The cyclic voltammetry of oxygen cannot be used to estimate the true reduction potential of oxygen as it is an irreversible process where O₂/O₂⁻ and O₂⁻/HO₂⁻ are not in equilibrium. However, the cyclic voltammetric wave reflects the charge transfer rates for the reduction of oxygen.

The deposition of metals such as Pd and Ag onto carbon nanotubes significantly shifts the above peaks anodically. With 4.5 \(\mu\)g/cm\(^2\) of Pd deposited on the carbon nanotube electrode, the cyclic voltammetric peak potential \(E_{pc}\) is shifted to 0.07 V (in 1 M H\(_2\)SO\(_4\)). A much smaller shift is observed at the carbon paste electrode. The polarization curves at the carbon nanotube electrodes were recorded at a sweep rate of 2 mV/s with dissolved oxygen constantly being bubbled into the medium. Tafel plots were constructed following the established procedures. Results of the electrocatalysis of the above reaction using nanotube catalysts are summarized in Table 1. The exchange current densities shown are indications of how fast the reaction is taking place. The values for the current density in the acidic medium are compared for nanotubes, carbon paste, and a commercial fuel cell catalyst (Pt/C/Nafion). For the latter, values are lower since resistances are cumulative when supported by Nafion or other membranes, and hence are not directly comparable to the results here. Since the surface topology of the nanotubes can vary, the true active surface area (for current density determination) is estimated electrochemically, from the current–voltage curves and chronocoulamperometric recordings. We focus on the comparison between nanotubes and graphite, and the values of the current densities, which are at least five times higher for nanotubes (the trend is similar in acidic and neutral media). Figure 2 shows the cyclic voltammetric curves for the first reduction of oxygen at the nanotube electrode, in acid medium, being compared to the same for carbon paste electrodes under similar conditions. The peak current at the nanotube electrode increases with sweep rate and follows the diffusion-controlled process. The second reduction peak of oxygen is situated beyond the first peak before the background limit. At this stage, oxygen reduction proceeds to water by a four-electron process. At the carbon paste electrode these peaks are shifted towards more negative potentials and are ill defined. Also note that the background curve at the carbon nanotube electrode is shifted anodically compared to the carbon paste electrode. The diffusion coefficient of oxygen in the reaction is determined (using potential step electrolysis at \(-0.6\) V) to be \(3.1 \times 10^{-5}\) cm\(^2\)/s compared to a similar reported literature value of \(2.6 \times 10^{-5}\) cm\(^2\)/s. We have also studied metal (e.g., Ag, Pd) deposited nanotube electrodes and preliminary data suggest that the exchange currents at metal/nanotube electrodes are much higher than those observed for metals on graphite or glassy carbon electrodes. The latter systems have been tested extensively for improved electrode performance of fuel cells. Very recently, pyrolic nanotube membranes made using ceramic templates and deposited with metal catalysts have been reported to catalyze the oxygen reduction reaction.

To understand the microscopic mechanism of electron transfer on nanotubes, we performed ab initio density-functional-theory calculations and molecular dynamics (MD) simulations. Here we discuss the adsorptive dissociation of oxygen on the carbon nanotube surface and the charge transfer process, concentrating on Reaction 1 given above. A complete understanding of the former needs a more detailed study concerning the activation energies and the rates of dissociation. However, assuming that the dissociation of the O\(_2\) molecule takes place (preliminary MD simulations suggest this), we look for the minimum energy of a single atom located close to the regular lattice sites (hexa-

Table 1. Comparative data for the electrocatalysis of oxygen reduction at carbon nanotubes and graphite paste electrodes in acidic and neutral media. \(i_0\) is obtained from the intercept of the overpotential vs. log (current density) plot. It represents the rate constant for the electron transfer process. The values reported are all for room temperature and averages from several experiments. The first three values are from the present work whereas the last \([17]\) is a literature value \([18]\).

<table>
<thead>
<tr>
<th>Electrode reference material</th>
<th>Exchange current density (i_0) [A/cm(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotubes</td>
<td>6.3 \times 10^{-4}</td>
</tr>
<tr>
<td>H(_2)SO(_4) (pH 2)</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>1.2 \times 10^{-4}</td>
</tr>
<tr>
<td>H(_2)SO(_4) (pH 2)</td>
<td></td>
</tr>
<tr>
<td>Carbon nanotubes/Pd (0.08 mg/cm(^2))</td>
<td>36.6</td>
</tr>
<tr>
<td>H(_2)SO(_4) (pH 2)</td>
<td></td>
</tr>
<tr>
<td>Pt/C/Nafion (Commercial)</td>
<td>1.09 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Fig. 2. Current–voltage curves for the electrocatalysis of dissolved oxygen at carbon nanotube and carbon paste electrodes. Medium is H\(_2\)SO\(_4\) (pH 2): 1) background with carbon paste (no oxygen); 2) background with carbon nanotubes (no oxygen); 3) with dissolved oxygen (~1 mM) at the carbon paste; 4) with dissolved oxygen (~1 mM) at the nanotubes. The recordings were all done at a sweep rate of 100 mV/s.
gons) and defects (pentagons and heptagons) on the nanotube surface. Then we compute the trapping of electrons by the oxygen atom on the tube-wall surface, which subsequently leads to the interaction of the negatively charged atoms with protons to form H₂O₂.

We describe the interaction between valence electrons and ionic cores by non-local norm-conserving pseudopotentials for C and O[23] with a 60 Ry energy cutoff for the plane-wave expansion of the wavefunctions. We work within periodic boundary conditions by keeping the minimum distance between tubes (or sheets) as 5.5 Å to ensure negligible interaction. The ground-state geometry is obtained by minimizing the Hellmann–Feynman forces. The computed C–C and C–O bond lengths for graphite and C₆₀ structures (1.42, 1.40, and 1.46 Å, respectively) and molecules (C-dimer, CO and CO₂) agree with experimental values within 1%. The forces acting on the atoms are derived from the corresponding electronic ground state, which is accurately described within the local-spin-density approximation.

As a first step, we determined the static (T = 0) equilibrium atomic positions and the corresponding Mulliken population analysis for a single oxygen atom impurity sitting on a perfect and defective graphene sheet and a SW nanotube for various initial positions: hexagonal sites and defects (pentagons and heptagons). We used a basis set of localized 2s–2p pseudoatom orbitals for C and O in order to carry out the Mulliken orbital populations analysis (atomic and bond charges are easily obtained in this basis set representation). Within this scheme we have a consistent and accurate way of comparing the charge transfer to the oxygen atom in different environments, although the absolute values are not representative of the formal oxidation number.

In Figure 3a we show a typical bond-rotation defect of a (6,6) SW carbon nanotube[24] and the corresponding simulated three-dimensional local density of states[25] for occupied states close to the Fermi level. All nanotubes were relaxed to their equilibrium geometries before oxygen approached them. The calculations for a closed (6,6) carbon tube were performed on tubular nanotube sections terminated on one side by H atoms that saturate the bonding of the two-coordinated C-atoms, and on the other side by fullerene-like caps with a six-fold rotation symmetry (Fig. 3b). It is clearly seen that due to the higher density of states at the pentagonal sites, these would act as electrophilic reaction sites. The same behavior is obtained at the nanotube tips and nanoparticles where pentagons are present.[26] Oxygen reduction with a larger charge transfer takes place at these high density of states sites. The analysis of the Mulliken partition shows an ionic local environment for the oxygen atom. We take as reference the charge...
transfer for a perfect graphene sheet. For the SW nanotubes, the calculations show that curvature leads to a slightly larger charge transfer that tends as 1/D (D is tube diameter) to the graphitic values (2 % larger for the (6,6) nanotube with D = 0.82 nm). This slight increase is attributed to curvature-induced σ-π hybridization that alters the energy band dispersion close to the Fermi level.\(^\text{[2]}\) The average Mulliken population at a pentagon is 3–4 times larger than at a graphene hexagon in both planar and tubular structures. Furthermore, the computed distance between negatively charged oxygen and the closest surface carbon atom on the nanotube (~1.8 Å) is larger than any molecular C–O bond length, indicating the lack of bond formation between carbon and oxygen. Atomic oxygen preferentially sits on the defect sites, producing a region with very large local density of states (Fig. 3b) that could be easily reduced by protons in the solution.

We have performed room temperature MD simulations for the deposition of an O\(_2\) molecule on a defective graphite sheet in order to assess the reliability of the single atom model described here. The main result is the fact that the O\(_2\) molecule acquires a negative charge on approaching the surface, then stays on the surface and after some picoseconds starts slowly to dissociate. Also, the first indication is that the defects tend to activate the dissociation of the O\(_2\) molecule. This validates oxygen reduction taking place through charge transfer to atomic oxygen, which is an intermediate transition state for the negatively charged oxygen species.

The calculations indicate that pentagons at the nanotube tips, pentagon–heptagon defect pairs in the lattice, and, to a lesser extent, curvature are responsible for the improved activation behavior of oxygen reduction. It has been seen that surfaces of as-grown multiwalled nanotubes contain large numbers of defects, which are removed only by high temperature annealing treatment.\(^\text{[3]}\) The improved catalytic behavior of nanotube electrodes was evidenced previously in bio-electrochemical studies.\(^\text{[4]}\) Our new results here confirm the potential of using nanotubes in electroactive applications such as fuel cells. The low density of nanotubes should be an added advantage in these applications.

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[17] The commercial catalyst corresponds to Pt on carbon (20 % Pt/C) with loadings of 0.4 mg/cm\(^2\) on 125 μm Nafion Dupont membranes. The conditions for the reaction using the commercial catalyst are quite different and not comparable to experiments performed here. Commercial carbon electrodes are three-phase electrodes: gas, liquid, and solid. They typically contain a hydrophobic membrane or binder attached to the carbon electrode. Due to the limited solubility of oxygen in the medium the output current will not be high as compared to the reduction on the carbon nanotube or carbon paste electrodes as reported here, where direct molecular oxygen approach is possible. This will result in differences in the charge transfer rates and exchange current density values. The value for the commercial catalyst is merely to show the acceptable limits for operation of a commercial cell.
[19] The true active surface area used to estimate exchange current density is estimated from the current–voltage curve in cyclic voltammetry of 5 mM K\(_4\)Fe(CN)\(_6\), and the chronoamperometric recordings. Using the peak current or the slope of the Cottrell’s plot the area of the electrode is calculated with the diffusion coefficient of K\(_4\)Fe(CN)\(_6\) as D = 0.76 × 10\(^{-5}\) cm\(^2\)/s and the number of electrons taking part in the reaction, n = 1 \([11]\).
[25] The 3D local density of states is computed within an energy window of 0.8 V where we collect information from the states close to the Fermi level that are relevant for the reduction process studied here.
[27] The curvature- (to a lesser extent) and defect-induced metallization and the edge-free structure could explain the improved charge transfer and catalysis of nanotubes, compared to other carbons.

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See page 87 for ordering details.