QUANTUM MECHANICAL DESCRIPTION OF CATALYTIC PROCESSES AT THE ELECTRODES OF LOW-TEMPERATURE HYDROGEN-OXYGEN FUEL CELLS

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Abstract: The functioning of a hydrogen-oxygen fuel cell near its catalyst-covered electrodes is studied using quantum chemistry methods. The role of charge transfers in controlling the capture and release of reagents at the catalyst surfaces is shown to be decisive. Also avoiding build-up of water on the electrodes is demonstrated to depend on charge transfer at the electrodes.

1. Introduction

The overall structure of a proton-exchange-membrane (PEM) fuel cell is depicted in Figure 1. In qualitative terms, the processes involved in producing electric power from the flow into the cell of hydrogen and oxygen may be described as follows:

Molecular hydrogen and molecular oxygen is dissociated at the negative and the positive electrode surfaces, with the help of a catalyst such as Ni or Pt. The hydrogen atoms chemisorbed to the negative catalyst surface loose their electrons and move away from the surface, into the membrane structure and further to the positive electrode region. An electric potential gradient is required to accomplish this transport, and it is indeed formed, as the electrons lost at the negative electrode travel through an external circuit (where work is delivered) to the positive electrode. In case of an open circuit, the protons would not be able to move into the membrane unassisted. The components important for studying the reactions at the negative electrode surface are shown at the top of Figure 2, while those important at the positive electrode are in the middle.

The protons enter high above the surface of the catalyst at the positive electrode with oxygen atoms chemisorbed to it. The subsequent processes include motion of protons (hydrogen atoms with charge +1) to the catalyst surface, combination with oxygen atoms, forming first OH groups and subsequently, by capturing a second proton, water. The succession of process steps and the charge distribution for each intermediary configuration has been the subject of both speculation and attempts of calculation [1-5]. One important question is for how many of the process steps an electric potential gradient is required. According to [1], it is certainly necessary for allowing the water molecules formed to leave the catalyst surface. In any case, the electrons having travelled through the external circuit must reach the catalyst surface and

jump to the adsorbed oxygen and hydrogen complex during some of its reaction steps, in order be able to end up with neutral water molecules. Figure 3 shows the likely potential energy and current-voltage characteristics.
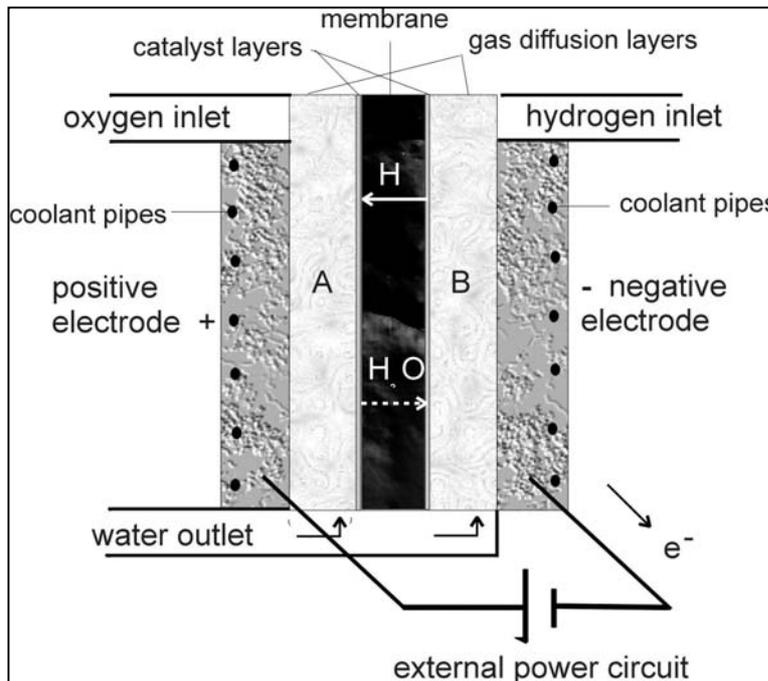

Figure 1. Schematic layout of a PEM fuel cell. Transport through the membrane is indicated in the middle layer. On each side of it there is a catalyst layer, also in contact with the gas diffusion channels and the outer electrically conducting leads shown in the graph. Sometimes, the catalyst assembly is itself termed as part of the electrode [1].

Figure 2. Sketch of the parts of the fuel cell included in the negative-electrode calculation (top) and the positive-electrode calculation (middle). The bottom panel indicates the role of the external circuit and suggests the performance of separate calculations for different total electrode charges. Numbers shown are for the processes corresponding to the involvement of a single oxygen molecule (and hence two hydrogen molecules).
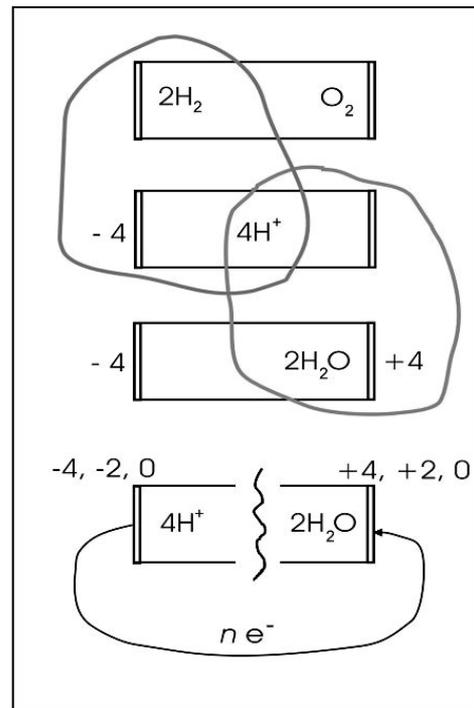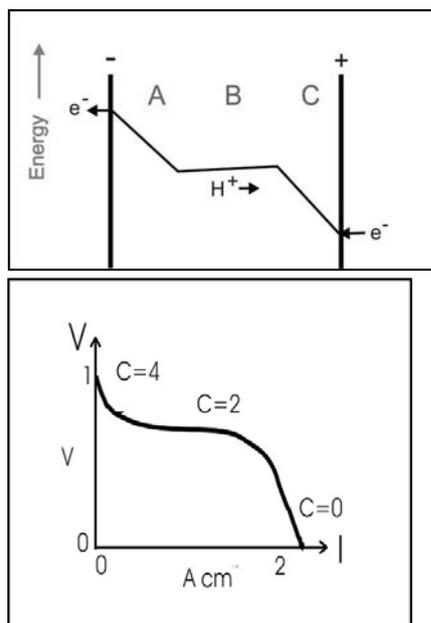

Figure 3. Potential energy felt by proton moving from negative (A) to positive (C) electrode (top), and current-voltage (IV-)diagram for the positive electrode (below). The charges C pertain to the system with two-oxygen atoms and four-hydrogen atoms considered in Figure 2.

2. Molecular level quantum calculations.

Although many of the features of PEM fuel cell reactions can be understood by qualitative arguments, specific problems e.g of water management or upstart times will benefit from calculations on a molecular level. The first such quantum chemistry calculations were made for the dissociation processes at the catalyst surfaces, starting with the easier negative electrode [6] and proceeding to the positive one [7]. A simple, but realistic version of these calculations using density functional theory are shown in Figs. 4 and 5, for a nickel catalyst surface. The calculation for the more efficient catalyst platinum would be similar, but more time consuming. The process of passing protons through a membrane allowing this but not penetration of molecular hydrogen is making use of polymers such as Nafion (a Dupont de Nemours trademark) or similar substances. The detailed nature of the membrane structure is not completely known, although the basic molecular unit characterising Nafion is [1]. Figure 6 shows the result of a first orientation in optimising the bulk shape by quantum methods (i.e. calculating the configuration of lowest energy). Two minima of equal depths are found for a periodic 2-layer structure with the known basic unit structure – one with the backbone layers adjacent and one with them apart, suggesting alternate layering. However, this is not what is indicated by the low-resolution spectral analyses made [8], which rather suggests a number of nodules of round shapes, each of which may of course consist of two or more alternating layers with backbone layers on the outside.
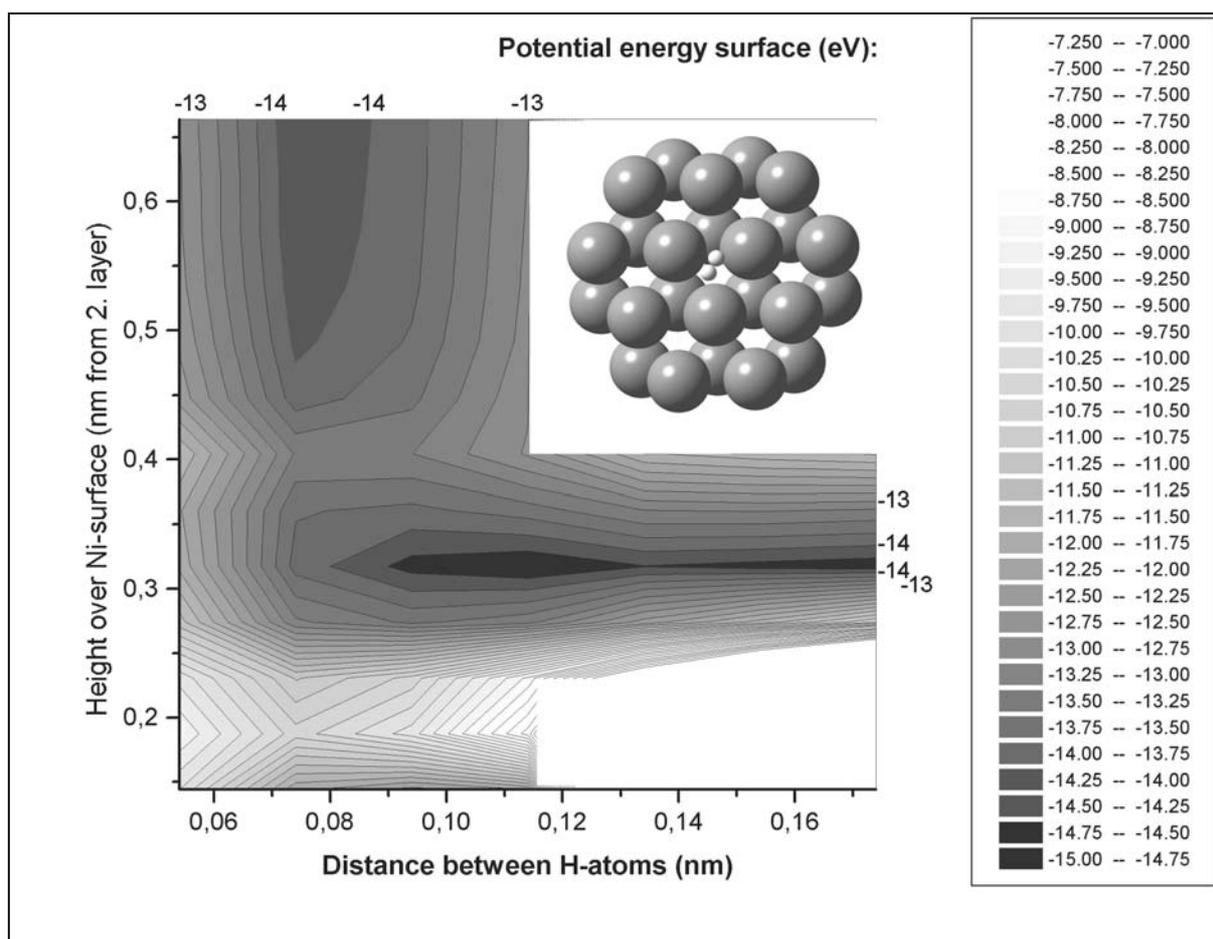

Figure 4. Dissociation of a hydrogen molecule at a nickel surface. The geometry is shown in the insert. The intermediate barrier is overcome by kinetic energy or by quantum tunnelling, after which the H—H distance is increased to at least twice the molecular value [1].
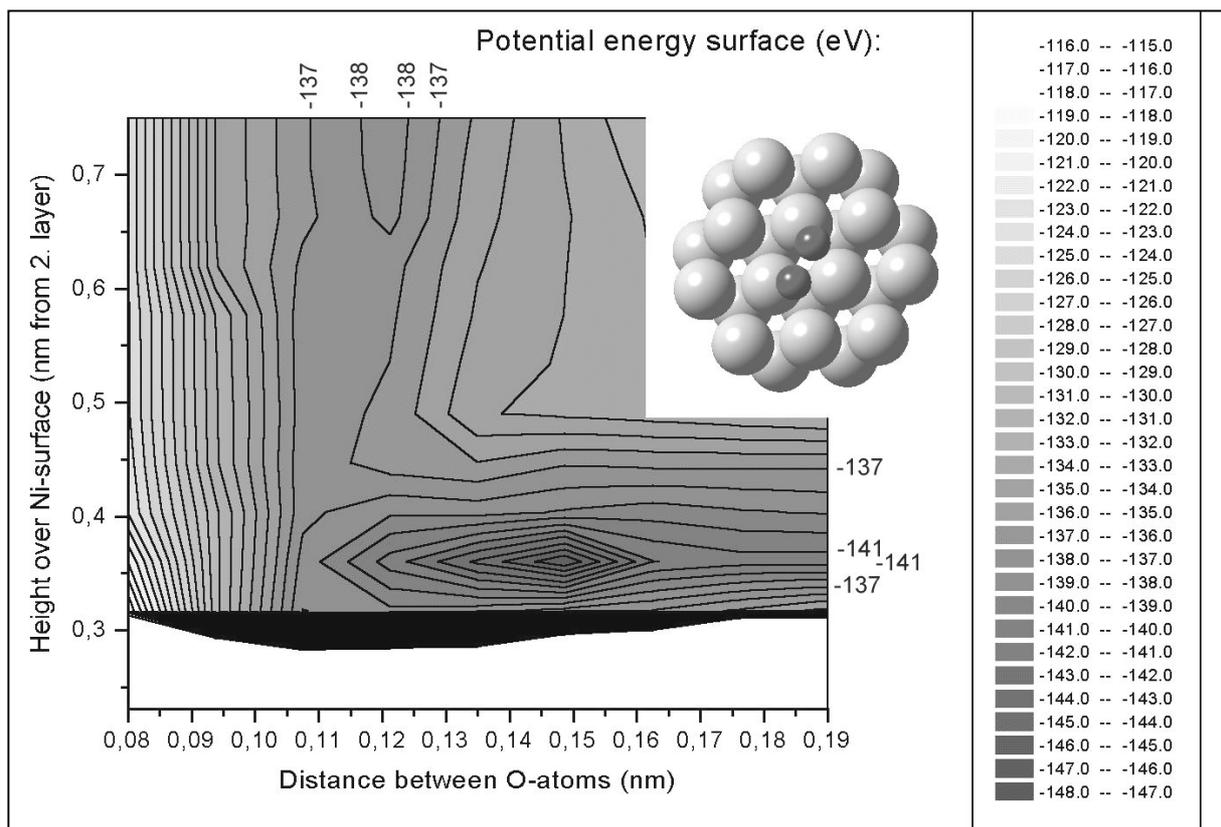
Figure 5. Dissociation of an oxygen molecule at a nickel surface. The geometry is shown in the insert. The intermediate barrier is overcome by kinetic energy or by quantum tunnelling, after which the O—O distance is increased to at least 1.5 times the molecular value [1].
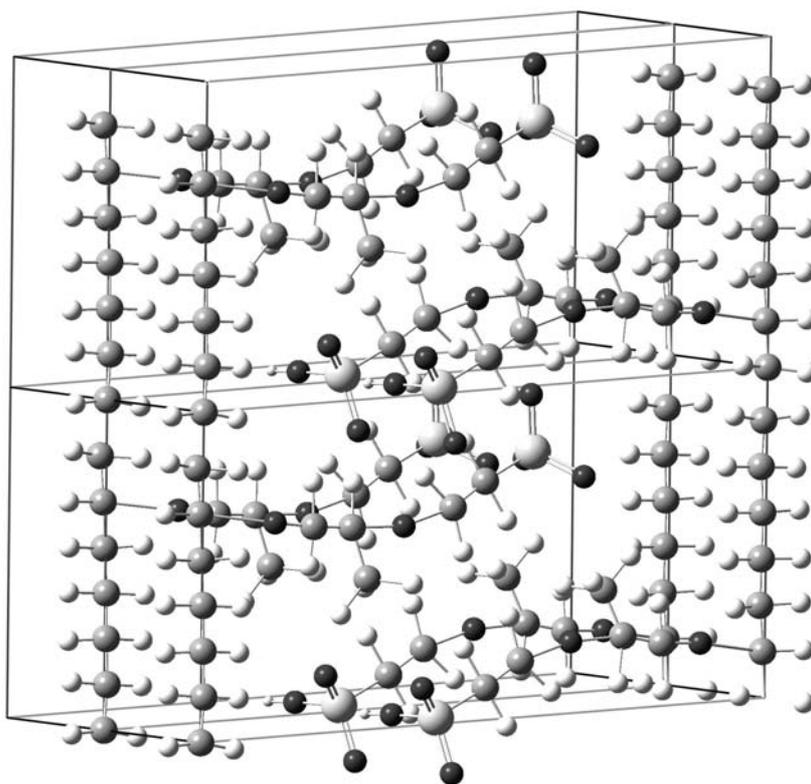

Figure 6. Possible structure of the Nafion membrane containing lengthwise fluorocarbon polymers and side chain extrusions with sulphonic acid endpoints. There is room for inner presence of water molecules, which may facilitate the transport of protons (H^+).

3. Positive electrode/catalyst investigations.

The investigation of the water-forming processes at the positive electrode and its catalyst starts with 4 protons situated far above a catalyst surface (Ni in the calculation) where 2 oxygen atoms are already chemisorbed after a dissociation of the kind modelled in Figure 5. It is clear that a full determination of the potential energy as function of the configuration coordinates of all 6 particles outside the Ni-surface is prohibitive (and adding the possible displacement of surface Ni-atoms even more). Some investigators simply postulate the reaction steps on the basis of classical ionic and complex reactant chemistry (9), but that rather deceits the purpose of quantum calculations, which is to explore the reaction mechanisms beyond the ball-and-stick type chemistry models. The approach taken here is to combine optimisation routines with limited potential energy scans. The method of optimisation calculates potential energy gradients at each step and proceeds in the direction (in parameter space) of steepest descent. Figure 7 shows an example of such a set of calculations, for the case where each oxygen atom has already captured one hydrogen atom (that process is the straightforward result of a preceding optimisation). The second set of protons moves along a descending potential energy surface but then stops about halfway to the region where the OH structures are. Figure 7 shows that the potential surface simply becomes flat. To move the protons further requires either a change in the configuration or possibly that a potential barrier has to be overcome (as in the dissociation cases, Figures 4 and 5). The way to proceed is now a potential scan, i.e. the determination of the potential energy for a mesh of configuration coordinate values (those coordinates deemed interesting). This will show if there are deeper minima on the other sides of potential energy barriers. Once across a barrier, another run of optimisation may
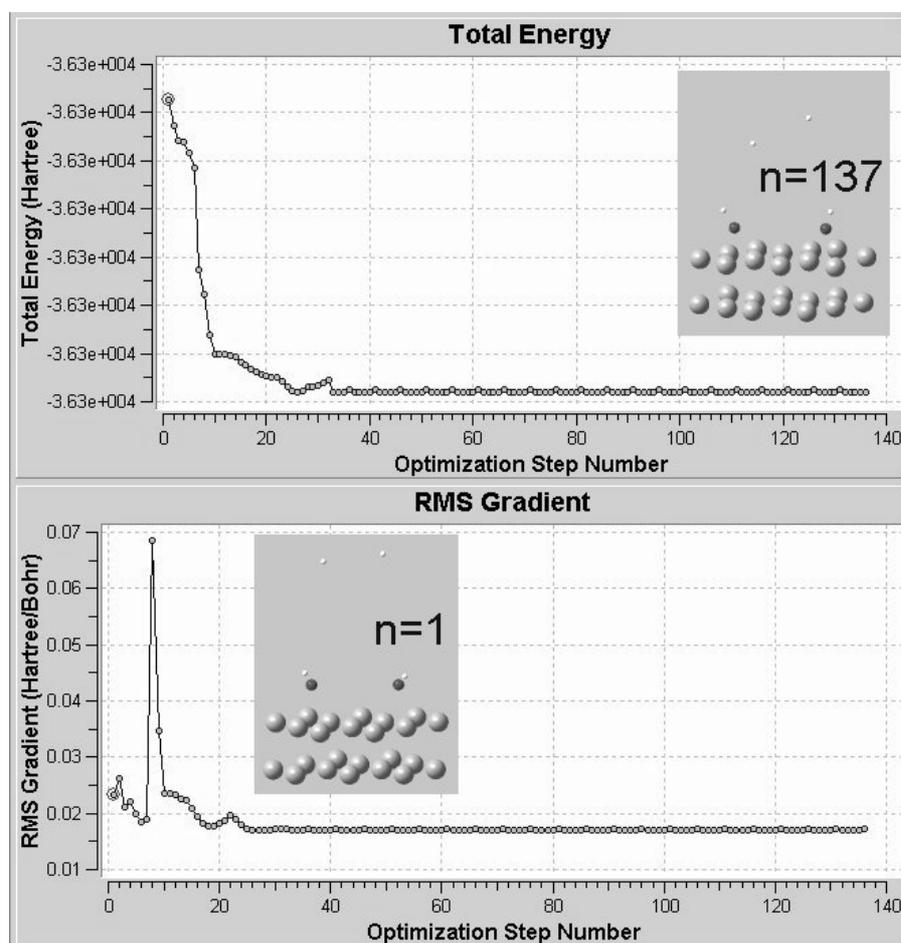

Figure 7. Potential energy and its gradient in the direction taken along an optimisation path, for two OH and two H atoms outside a Ni catalyst surface.

be carried out, and so on – until the final situation is reached, with two hydrogen atoms combining with each oxygen atom and forming water that should be demonstrated to be able to detach from the catalyst surface and move away.
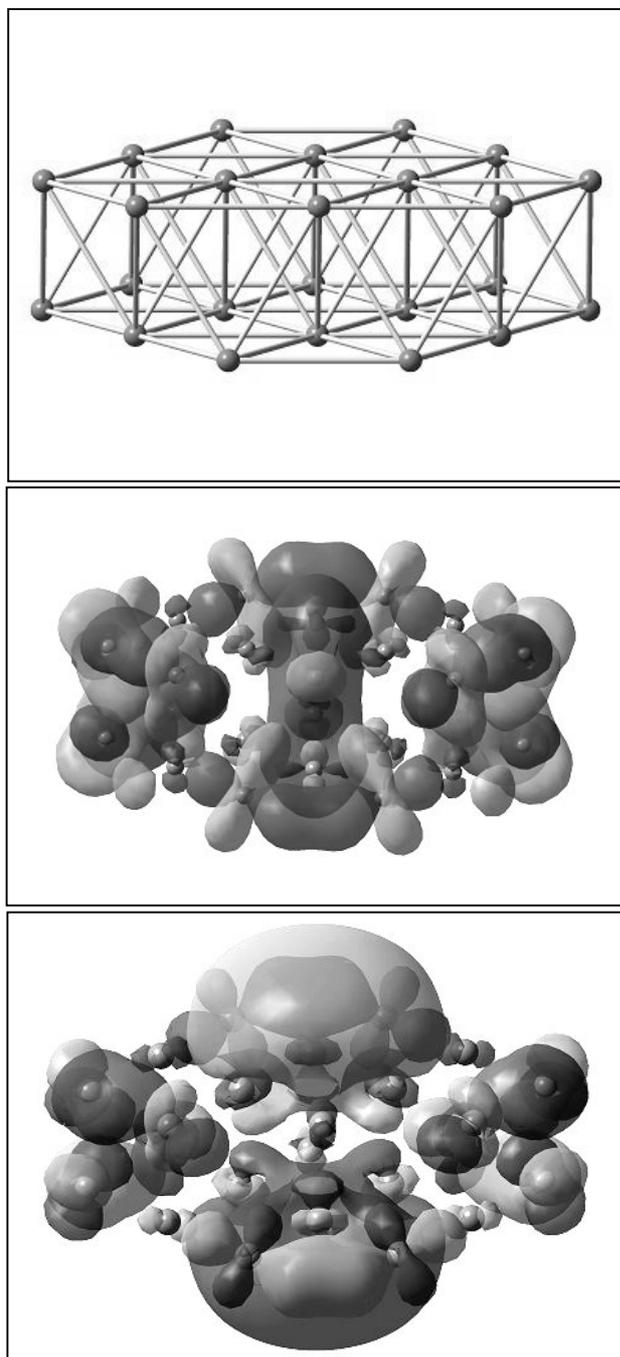
Figure 8. DFT (density functional theory) quantum calculation for a chunk of the Ni catalyst alone. The 24 atoms included are in the configuration shown at top. The electron density of the highest occupied molecular orbital (HOMO) is shown in the middle, and that of the lowest unoccupied orbital (LUMO) at the bottom. The two shades of grey denotes the sign of the wave function, while the contour delimits the volume, inside which the absolute square of the wave function is larger than 0.004. It is seen that the LUMO orbital, into which a newly arriving electron would have to go, has a large volume extending out of the catalyst surface. This supports the ability of the catalyst to assist water formation near the surface, by delivering the excess electrons needed to transform the positive structures above the surface (from the four H^+ ions) into neutral water. The electrons for this task are the ones delivered through the external circuit.

Figure 8 illustrates the orbitals of the catalyst (here Ni). It is seen that some of the extra electrons coming from the external circuit (Figure 2) would likely go into molecular states with a wave function density stretching out in the region, where the oxygen is chemisorbed and where the protons can be attracted precisely by the extra negative charge of such surface-based electrons. A systematic picture of the reaction steps involved in the water formation is shown in Figure 9. This part of the modelling effort has been discussed previously [1-5]. The catalyst is in Figure 9 still modelled as just two layers of Ni, and the surface reactions are de-

scribed by density functional theory using the B3LYP potential and an SV basis [1]. However, where the early calculations left it to the quantum chemical calculation to correctly distribute charges, the present work uses a splitting of the system into subsystems each with prescribed charge, and estimates the total energy by use of the ONIOM technique [10]. Furthermore, the general behaviour of the charge distribution near the catalyst surface is known (from experiments such as [11]) to change as the current in the external circuit increases from zero (open circuit) to its maximum value. Therefore, the quantum calculation is repeated for total charges varying from +4 (because two water molecules are formed in the model) to zero, simulating increasing external currents.
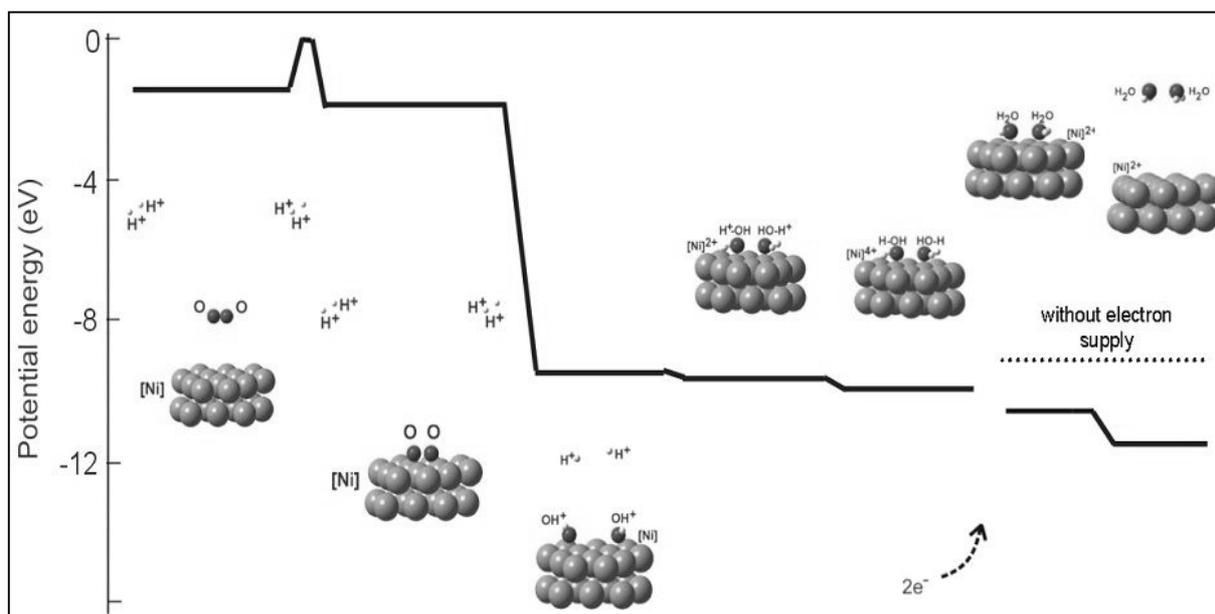

Figure 9. Selected stages en route to the formation and release of water at the positive electrode of a PEM fuel cell. The energy scale is adjusted for the binding energy of two additional electrons in the two rightmost columns. The calculated ΔE_{pot} from column 2 to column 3 considerably exceeds the experimental value [1].

Figure 9 shows that the energy gained by capturing the first two protons is greatly overestimated. This is a well-known problem of DFT calculations comparing situations with some part of the structure (here 4 H$^+$) separated from the rest with a situation where all atoms are part of the same structure [1]. It is further seen, that the process continues until a water precursor is formed (with one set of hydrogen atoms further away than in a water molecule) and the 4 positive charges are transferred to the Ni structure. At this point the external current is invoked, which is seen (in the two rightmost columns) to allow regular water molecules to form and to move away from the catalyst surface.

For a neutral catalyst, only one of the two water molecules formed is able to leave the catalyst surface, although both water molecules can move laterally along the catalyst surface [1]. When the electric current is switched on, the situation changes, as shown in Figure 10. However, the second water molecule still has difficulties leaving the surface at half current (C = +2 in the simple case of only 4 charges considered), and only at C = 0 does the second water molecule leave the surface easily. This implies that water management in a PEM fuel cell is dependent on establishing a strong current and that a partially functioning cell may experience

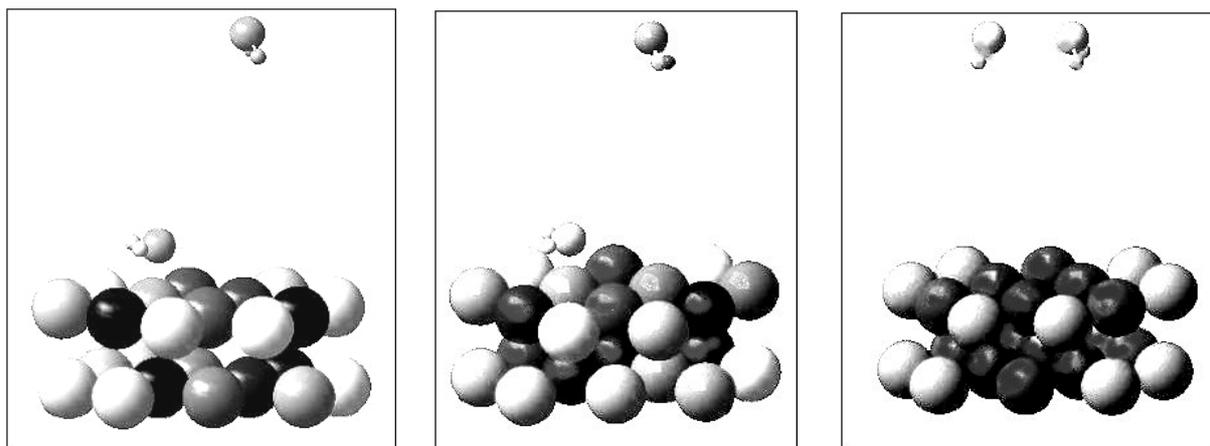problems of water accumulation at the positive electrode surfaces (making further water formation difficult).

Figure 10. Atomic charge distribution on atoms ("Mulliken charges") for calculations with overall charge set at +4 (left), +2 (middle) and 0 (right). The darkest grey corresponds to a charge of –0.6 on the atom, and the lightest to 0+0.6.
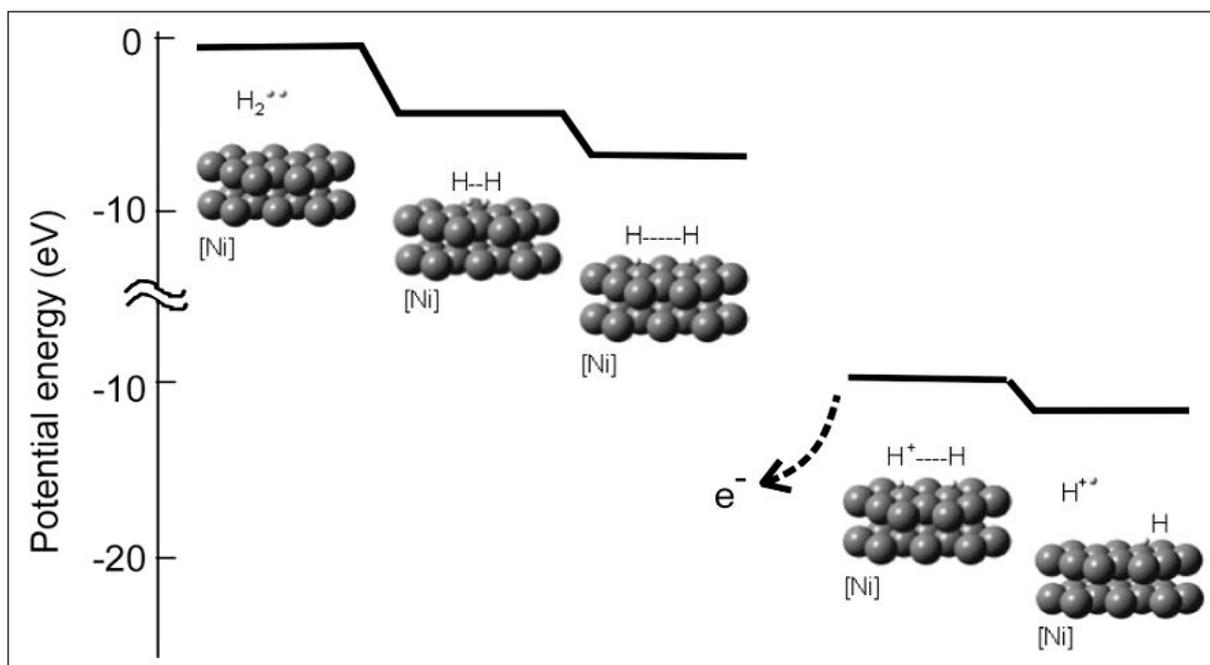

Figure 11. Selected stages en route to the hydrogen dissociation and hydrogen-ion release from the negative electrode of a PEM fuel cell. The energy scale is adjusted for the binding energy of one lost electron in the two rightmost columns, but due to spin change, the absolute energy change from column 3 to 4 cannot be calculated accurately with the ONIOM method.

4. Negative electrode/catalyst behaviour

Following the dissociation of hydrogen molecules at the negative electrode/catalyst (as shown in Figure 4), the detachment of the chemisorbed protons may be investigated by a procedure analogous to the one used at the positive electrode. The corresponding ONIOM calculation requires only a division of the system into two components: the Ni lattice as the lower layer and the H-atoms as the upper layer (just two of the 4 H's need to be included). Calculated potential energy values shown in Figure 11, for an overall charge starting at zero but increas-

ing to +1, allow one hydrogen ion to escape from the surface, while its electron has been transferred to the external circuit through the metal catalyst electrode. Expelling both H+-ions in one step is found energetically less favoured. The ONIOM multi-layer calculations presented in Figure 11 have a problem with keeping track of total spin, the conservation of which is not rigorously enforced by the program code, and it therefore may deviate from the correct one, sometimes causing absolute energies to be unreliable. This happens when the spin of the included system components changes, here from zero to ½. However, the relative energies for similar configurations should still be reliable.

5. Concluding remarks

It is clear that for computational reasons, variations of position variables for the potential scans have to be restricted, as in the positive electrode case, where the 18 position variables of the four H and two O atoms (assuming the Ni-atom positions fixed) would require at least say 10 values of each of the 18 parameters in order to create a crude potential surface.

The investigation of fuel cell processes on a quantum level is clearly a continuously ongoing task, with each series of calculations revealing new sides of the problem studied. The achievement to date gives a rudimentary understanding of the mechanism of fuel cell operation on a quantum mechanical level, which is certainly a novel accomplishment. Still, there are many limitations inherent in the necessarily approximate methods used, and assuring each result to be reliable requires a multitude of control calculations to be performed. For this reason the work has to be continued, with particular emphasis on the areas where the conclusions turned out particularly sensitive to details of assumptions made in carrying out the modelling.

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