

# Overview of PEM fuel cell processes

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## Abstract

*Optimisation of fuel cell design requires a detailed understanding of the processes taking place at each electrode with the help of selected catalysts. A full quantum mechanical calculation of the processes at both the positive and the negative electrode of PEM cells is presented here. It provides an understanding of the attraction of hydrogen and oxygen to the respective catalyst surfaces, followed by dissociation and in the case of hydrogen the transfer of electrons to the electrode/catalyst surface, followed by a change in electrostatic potential allowing the hydrogen ions to move away from the surface and into the membrane structure. On the oxygen side, the dissociation is followed by a number of chemical reactions, whereby the hydrogen and oxygen atoms are combining first as ions and subsequently by transfer of electrons from the catalyst surface as neutral water molecules. In order to sustain electric current generation, the water molecules must be able to move away from the surface, which is shown to be allowed as a consequence of the reduction in electrostatic potential due to the external current. In other words, only when the external circuit is operating will the water molecules be able to leave the surface and avoid congestion.*

**Keywords:** *hydrogen, PEM fuel cell, quantum chemistry.*

## 1. Introduction

A model is used that describes the catalyst surface as two layers of Ni atoms, and surface reactions by density functional theory (DFT) using the B3LYP potential and an SV basis [1]. The Ni lattice is expected to serve similarly to Pt catalyst layers, but DFT calculations are quicker and more reliable, due to the lower electron shells in play. The system is split into three subsystems, each with prescribed charges, and the total energy estimated by use of the ONIOM technique [2]. The reason this is necessary is that the quantum system cannot from being given a total charge (+4 as 4 protons are moving from the negative to the positive electrode) know that the entire charge initially is sitting on the hydrogen atoms, is subsequently distributed among the hydrogen and oxygen atoms, and finally transferred to the underlying nickel surface. The calculations use a combination of restricted potential energy scans and local optimisations (see Figure 1).

## 2. Positive electrode reactions

Preliminary [1] and very preliminary [3] calculations for the positive electrode reac-

tions have been presented recently. Before that, only the dissociation of an oxygen molecule at a catalyst surface, and the corresponding hydrogen dissociation at the negative electrode catalyst, had been successfully described on a quantum chemical level [4]. Attempts to describe quantum mechanically the following steps of water formation at the catalyst, followed by the water being able to leave the surface, have previously failed to reproduce all the processes as a spontaneous chain of reactions producing an electric current in an external circuit [3,5]. Both for the density functional model calculations and for the case of extending molecular dynamics models [6,7], the likely reason is the lack of sufficiently detailed treatment of charge distribution issues. This is illustrated by the calculations shown in Figure 3, using a calculation based upon density functional theory with the PBE/PBE potential and SV basis, but with only the overall charge specified. Calculated charge distributions are grossly incorrect and only the chemisorbed states (to the right in the figure) could be improved by enlarging the Ni lattice.

The present work describes the processes from receiving four protons from the negative electrode through the membrane (corresponding to the case of a PEMFC), then during their interaction with a dissociated oxygen molecule and finally to the formation of water after receiving four electrons from the positive electrode catalyst (see Figure 2). The catalyst is still modelled as two layers of Ni, and the surface reactions are described by density functional theory using the B3LYP potential and an SV basis [1]. However, where early calculations left it to the quantum chemical calculation to correctly

distribute charges, the present work takes up the suggestion to use a splitting of the system into subsystems each with prescribed charge, and estimating the total energy by use of the ONIOM technique [2]. Furthermore, the general behaviour of the charge distribution near the catalyst surface is known (from experiments (such as [8]) 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.

The calculations used a combination of restricted potential energy scans and local optimisations. Figure 4 shows a favoured path of reactions with symmetry between the two OHH systems, showing the overall possibility of a spontaneous fuel cell reaction combining hydrogen and oxygen to water while building up a substantial electric potential for the external circuit power production. Similar behaviour is found for asymmetric cases, where one water molecule is formed and escapes before the other. The distribution of charges on atoms shown in Figure 5 illustrates the importance of charge distributions based on one model layer of ONIOM calculations, and includes asymmetrical reaction steps.

### 3. Negative electrode reactions.

The potential energy surface basis for dissociation of hydrogen molecules at a Ni catalyst surface was for the same lattice configuration as used here calculated in [1]. Extending this work by the corresponding 2-layer

ONIOM calculation with the Ni lattice as the lower layer and two H-atoms as the upper layer gives rise to the selected potential energy values shown in Figure 6, for an overall charge starting at zero but increasing to +1, which allows 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<sup>+</sup> ions in one step is found energetically less favoured. The current ONIOM multilayer calculations presented in Figure 6 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. In Figure 4, this happens when the spin of the included system components changes from zero to ½. However, the relative energies for similar configurations should still be reliable.

#### 4. Concluding remarks

The calculations described here were carried out on a small cluster of 3 GHz PC's and took several months of CPU time. Clearly the variations of variables had to be restricted, as even the 18 position variables of the four H and two O atoms (assuming the Ni-atom positions fixed) would require unrealistic computing times to produce just a crude potential energy surface based on say 10 values of each of the 18 parameters.

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.

#### References

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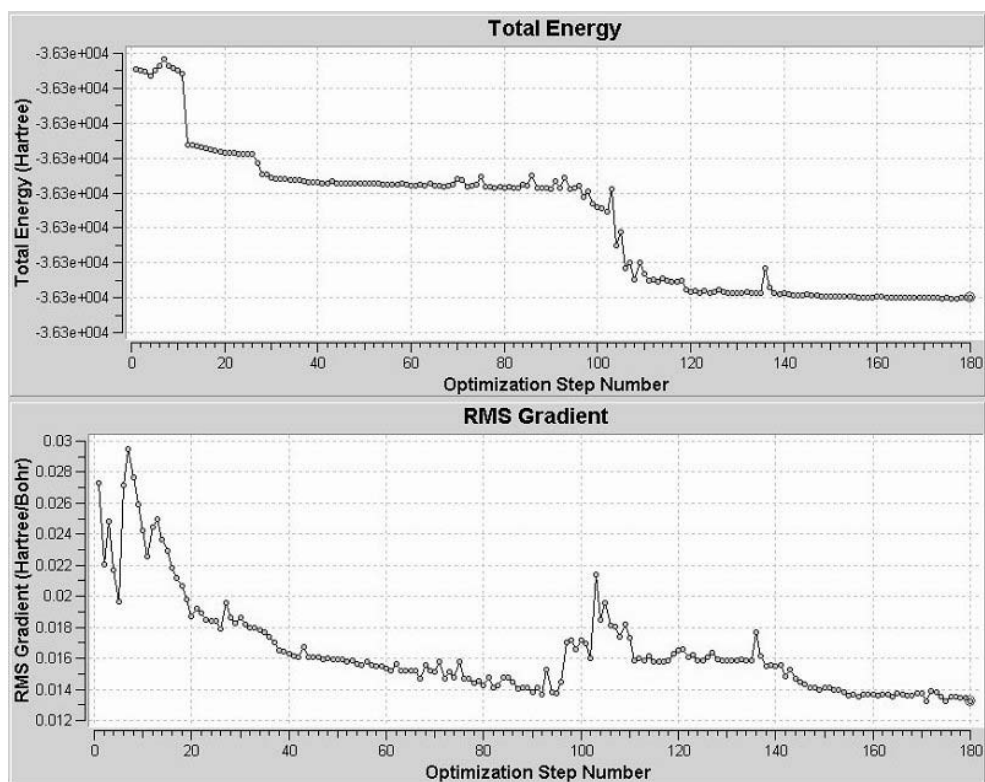


Figure 1. Approach to an optimised molecular configuration for one of the calculations of H and O atoms above a nickel surface. The minimisation of energy as function of iteration step is shown above, and the energy gradient at each optimisation step below.

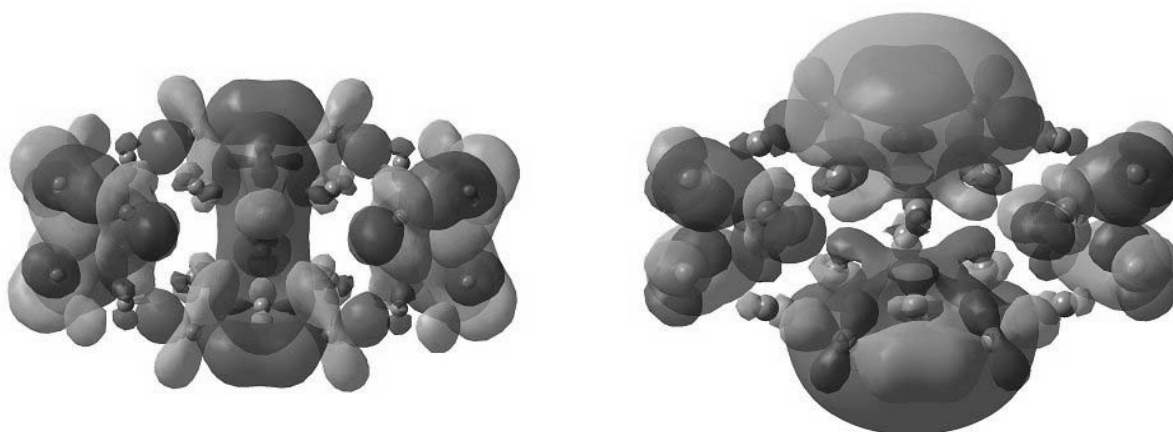


Figure 2. Electron density for the two nickel catalyst layers included in the calculation, either for the highest occupied molecular orbital (HOMO, left) or for the lowest unoccupied molecular orbital (LUMO, right). B3LYP density functional theory with an SV basis set was used. It is seen that the LUMO state offers a large electron density above the surface, as required for the fuel cell processes.

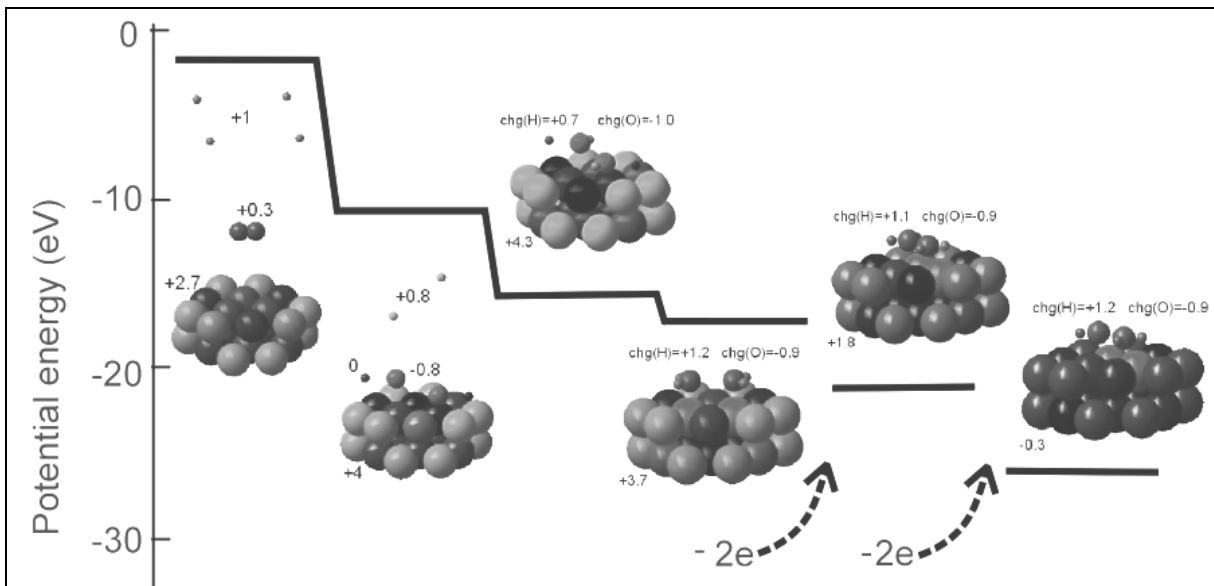


Figure 3. Early calculations for selected stages of hydrogen capture and water formation at the positive electrode of a PEM fuel cell. The four leftmost columns assumed a total charge of +4, while the rightmost columns assumed charges of +2 and 0. This type of calculation fails to place the 4 charges on the hydrogen atoms in the leftmost column, but increasingly does better when the atoms come closer together. Yet the energy differences between steps are usually too large [3].

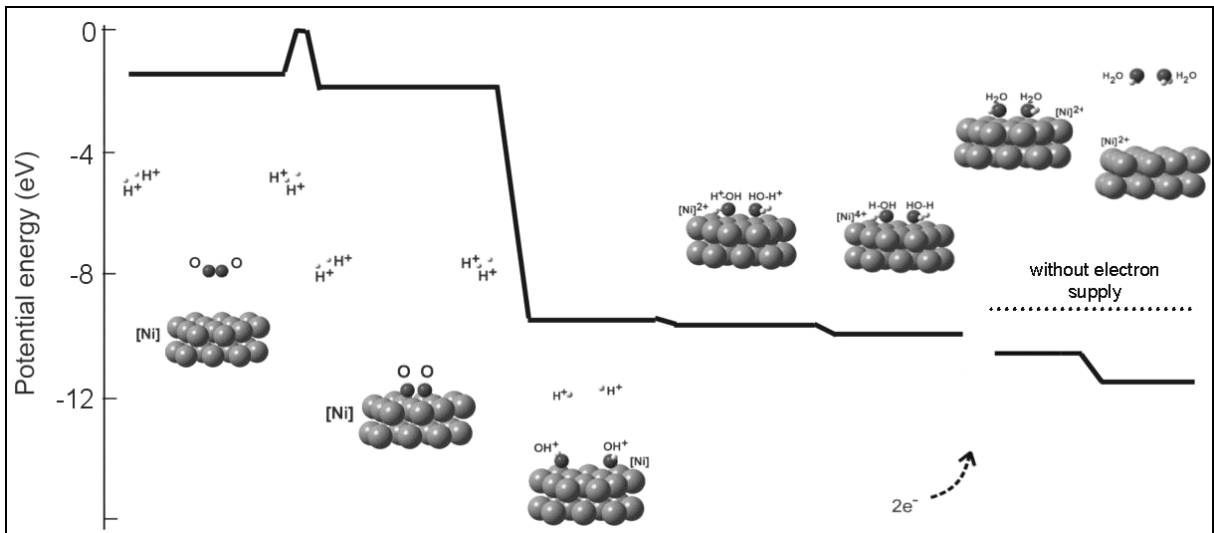


Figure 4. Selected stages en route to the formation and release of water at the positive electrode of a PEM fuel cell, from the present calculation. The energy scale is adjusted for the binding energy of two additional electrons in the two rightmost columns. The calculated  $\Delta E_{\text{pot}}$  from column 2 to column 3 considerably exceeds the experimental value [1].

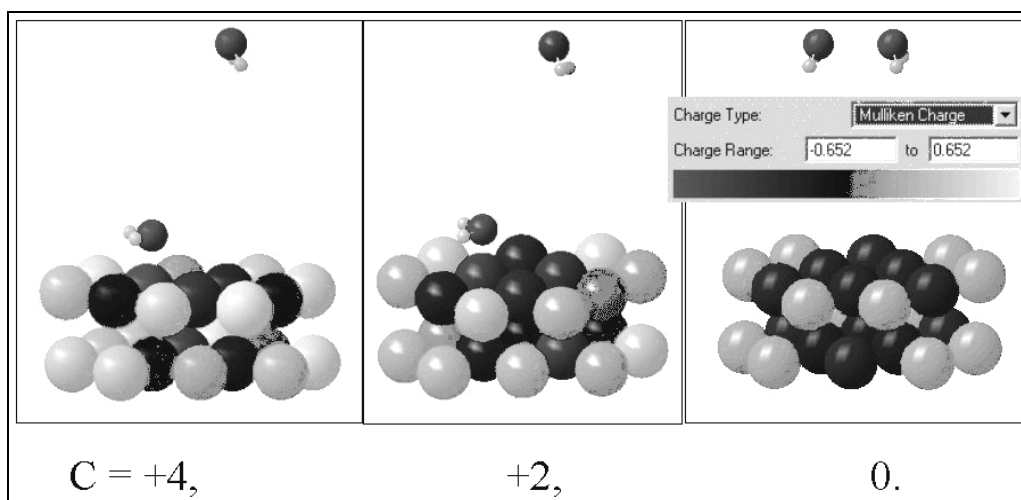


Figure 5. Atomic charge distribution for the total charge varying from 4 (open circuit) to 0 (maximum current), as emerging from the lowest model layer of calculations similar to the ones shown in Fig. 4.

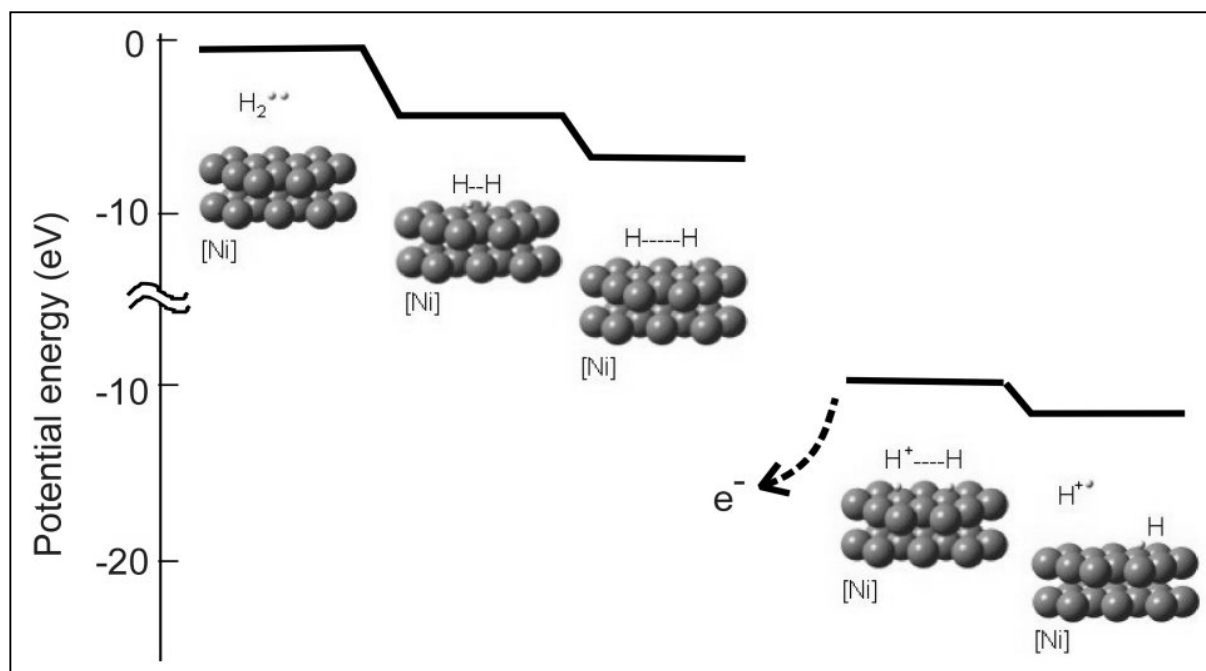


Figure 6. Selected stages en route to the hydrogen dissociation and hydrogen-ion release from the negative electrode of a PEM fuel cell. The energy scale is adjusted for the binding energy of one lost electron in the two rightmost columns, but due to spin change, the absolute energy change from column 3 to 4 cannot be calculated accurately with the ONIOM method.