



A combined experimental/theoretical approach to accelerated fuel cell development by quantitative prediction of redox potentials

Kakali Sen^{a,b}, Andrew Creeth^{c,d}, Sebastian Metz^{b,e,*}

^a School of Biological Sciences, University of Essex, Wivenhoe Park, Colchester, Essex, CO4 3SQ, UK

^b Scientific Computing Department, STFC Daresbury Laboratory, Sci-Tech Daresbury, Keckwick Lane, Daresbury, Cheshire, WA4 4AD, UK

^c ACAL Energy Ltd, The Heath Business and Technical Park, Runcorn, Cheshire, WA7 4QX, UK

^d AC Chemicals Systems Ltd, c/o Military House, 24 Castle Street, Chester, Cheshire, CH1 2DS, UK

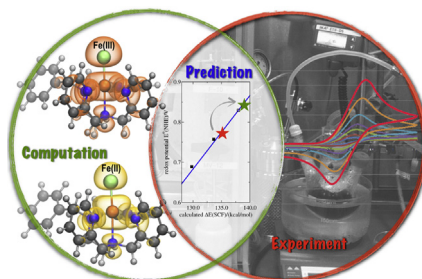
^e The Hartree Centre, STFC Laboratory, Sci-Tech Daresbury, Keckwick Lane, Daresbury, Cheshire, WA4 4AD, UK



HIGHLIGHTS

- Combined experimental/theoretical method to predict redox potentials of fuel cell catalysts.
- Highly accurate results for broad set of experimental conditions and reference electrodes.
- Simple side chain modifications allow improvement of open circuit voltage of up to 10%.
- Newly identified catalyst with even higher potential providing improvement of $\approx 25\%$.

GRAPHICAL ABSTRACT



ARTICLE INFO

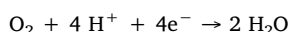
Keywords:

Redox potential
DFT
Solvent
Reference electrode
Performance optimization

ABSTRACT

This article presents a combined experimental/theoretical approach to accurately predict electrochemical redox potentials based on potential energy calculations. The approach works for experimental setups using different solvents and different reference electrodes and compensates for shortcomings in the prediction of redox potentials originating from the choice of DFT functional, basis set, and solvation model. The methodology is applied to two different sets of iron containing complexes which are used as redox catalysts in Chemically Regenerative Redox Fuel Cells (CRRFCs). For both sets of iron complexes with different 5 N donor ligands, an average deviation to the experimental values of $< 0.02\text{V}$ is obtained. Expectedly, the deviation is slightly larger with changes being made in the first coordination shell, but is still within the predictive limit. The scheme is then applied to obtain ligands with both improved properties and lowest production cost.

For the 21st century, fuel cells are regarded as one of the most promising approaches to efficiently convert chemical energy into electrical energy. Conventional Proton Exchange Membrane (PEM) fuel cells use precious metals like platinum to catalyze the oxygen reduction reaction at the cathode:



However, catalyst degradation and the cost of high Pt loading prevent the broader commercialization of fuel cells. Recently, very promising results were obtained by use of iron based molecular catalysts [1] in combination with a solution-phase redox mediator by means of a new flow-through cathode [2,3], see Fig. 1. Similar to the approach with molybdenum based polyoxoanions [4,5] the slow oxygen reduction reaction is performed in the bulk solution rather than on the surface of a precious metal electrocatalyst,

* Corresponding author. Scientific Computing Department, STFC Daresbury Laboratory, Sci-Tech Daresbury, Keckwick Lane, Daresbury, Cheshire, WA4 4AD, UK.
E-mail address: Sebastian.metz@stfc.ac.uk (S. Metz).

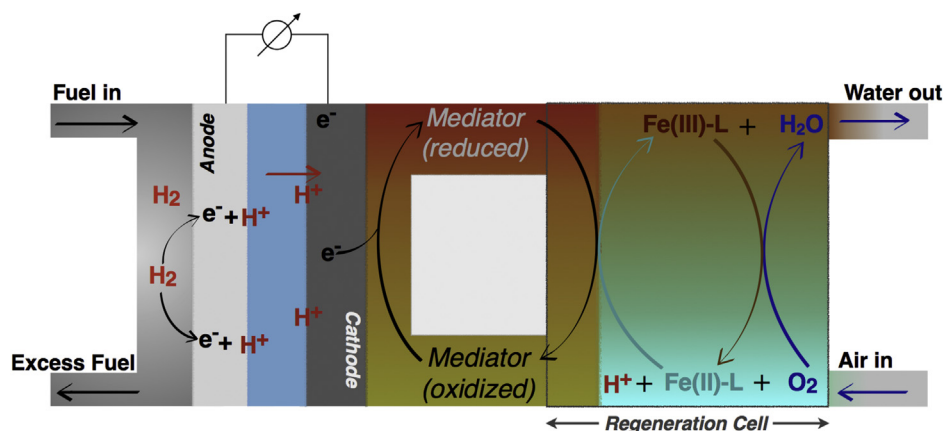


Fig. 1. Schematic working principle of a PEM fuel cell using the FlowCath[®] technology. Rather than reducing the oxygen at the cathode, an iron complex (Fe(II)L) is used as catalyst to reduce the oxygen with a mediator acting as electron source.

making it very flexible and adaptable when combining different molecular catalysts and mediators [6,7].

A key measurable parameter of catalysts and redox mediators, which relates directly to the voltage efficiency of the redox fuel cell, is the redox potential. Experimentally, the determination of a redox potential itself is a routine measurement, however the synthesis, optimization and purification processes can be very time consuming and costly. A fast, efficient and cheap method to predict accurately the redox potential, especially for smaller modifications of already synthesized complexes would significantly reduce experimental characterization of potential candidates and therefore reduce time to market. It should, however, be kept in mind that a high redox potential and therefore a high cell voltage does not necessarily guarantee a high power fuel cell performance, as this also needs a high current density. The latter, however, does not depend on the redox potential, but on the very complex electron transfer kinetics, which – among others – is influenced by factors like the rate of charge transfer between the cathode and the mediator or the mediator and the iron catalyst in its different intermediate states of oxygen reduction.

Applying computational modelling to predict redox potentials has a surprisingly long history. Already in 1949, Maccoll [8] applied the Hückel theory [9] to establish a correlation between the energies of the lowest unoccupied molecular orbital (LUMO) in conjugated organic molecules and their experimental redox potentials. Since then, more sophisticated quantum mechanical methodologies like density functional theory (DFT) have been applied to predict redox potentials using the Gibbs free energy of a redox couple, ΔG^0 , which is directly linked to the standard one-electron redox potential, E_{redox}^0 :

$$\Delta G^0 = -FE_{redox}^0 \quad (1)$$

The simplest approximation to calculate the change in the Gibbs free energy, ΔG^0 , is via frequency calculations of the optimized structures. It can then be obtained from the difference of the potential energy, $\Delta E(SCF)$, and several correction terms (zero point energy correction, $\Delta E(ZPE)$, thermal enthalpy correction, $\Delta H(thermal)$, and thermal entropy correction, $T\Delta S$).

$$\Delta G = \Delta H - T\Delta S = \Delta E(SCF) + \Delta E(ZPE) + \Delta H(thermal) - T\Delta S \quad (2)$$

However, this approximation introduces an unsystematic error and in addition, the frequency calculations, depending on the size of the molecules, can be computationally expensive compared to a normal geometry optimization procedure. On top, the choice of DFT functional, basis set, and solvation model influence the accuracy of the predictions [10–13] leading to too large deviations from the experimental values and therefore preventing an easy use as predictive model. To compensate for these shortcomings, several different computational approaches have been proposed as nicely outlined in the recent review by Truhlar and coworkers [11]. These methods, however, lack the simplicity to be used for screening molecules by non-theoreticians.

To approach the problem at hand with as little resources as possible, we took a combined experimental/theoretical approach: For our predictions, we rely on small, simple and fast potential energy calculations, $E(SCF)$, while substituting the more time consuming calculations by experimental values reported in the literature or from in-house measurements. It is significantly faster than the conventional approaches and therefore affordable for research groups without computational resources beyond a desktop PC e.g. within small and medium sized enterprises (SMEs). In addition, it predicts the redox potentials very accurately with R^2 values of 0.99, see below.

The rationale behind our approach is that for a class of very similar molecules, the correction terms in equation (2) are considered to be approximately constant, resulting in a correlation between the redox potential, E_{redox}^0 , and the corresponding potential energy, $\Delta E(SCF)$:

$$E_{redox}^0 \sim \Delta E(SCF) + const \quad (3)$$

In order to obtain the redox potentials relative to the normal hydrogen electrode $E^0(NHE)$, (or any other reference electrode) the values for the hydrogen half-reaction can also be included in the constant providing a correlation between the standard electrode potentials relative to the normal hydrogen electrode, $E^0(NHE)$, and the energy difference between two redox states of the investigated molecule, in our case between the Fe(II) and the Fe(III) states of the iron complexes:

$$E^0(NHE) \sim E(SCF, Fe(II)L) - E(SCF, Fe(III)L) + const \quad (4)$$

Of particular interest for this study were iron complexes with 5N donor ligands based on the trilen and the N4Py structures (Scheme 1). The starting geometries of the three complexes $[Fe(II)trilen(R = H/Cl/SO_3Na)-OH_2]^{2+}$ were obtained by manually substituting the functional groups of the ligand and exchanging Cl^- to H_2O in the crystal structure of $[Fe(II)trilen(R = H)-Cl]^+$ [14]. The same procedure was followed to generate the starting geometry of $[Fe(II)N4Py(R = H/CH_3)-OH_2]^{2+}$ from the crystal structure of $[Fe(II)N4Py(R = H)-Cl]^+$ [15]. Crystal structures for $[Fe(II)(Bz-tpen)-X]$ with $X = CH_3COO^-/OCN^-/Cl^-/SCN^-/Br^-/I^-/CH_3CN$ [16–18] and $[Fe(III)(Bz-tpen)-X]$ with $X = CH_3O^-$ [19] [20] were directly taken from the literature and were modified manually to obtain starting geometries for $X = OH^-/F^-$.

The initial structures were optimized using the B3LYP hybrid functional [21–26], which has been used for redox calculations [10,12,27,28]. The B3LYP functional is also known to correctly predict the lowest energy spin state of iron complexes [28,29] (see also supporting information for details), in combination with the def2-SVP basis set [30], which has also demonstrated to provide good geometries for transition metal complexes [31–33]. All calculations were performed using the ORCA software package [34]. Single point calculations were performed on top of the optimized geometries using the def2-TZVP basis set [30,35] together with the COSMO methodology [36] (using $\epsilon = 36.6$ for acetonitrile and $\epsilon = 80.4$ for water as solvent).

Download English Version:

<https://daneshyari.com/en/article/11005939>

Download Persian Version:

<https://daneshyari.com/article/11005939>

[Daneshyari.com](https://daneshyari.com)