

Direct Fuel Oxidation Alkaline Fuel Cells; The Kinetics of Borohydride Oxidation

Scott Nash^a, Fabrice Andrieux^a, Richard Dawson^{a*}, Hugh Sutherland^b,
Gene Lewis^b

^aEngineering Department Lancaster University, Lancaster LA1 4YR, UK

^bAFC Energy Plc, Unit 71.4 Dunsfold Park, Cranleigh, Surrey, GU6 8TB UK
r.dawson@lancaster.ac.uk

Alkaline based fuel cells are among the most efficient due to the enhanced kinetics of oxygen reduction in alkaline media. In space applications, they have demonstrated efficiencies near 60%, with the potential to generate electricity with efficiencies at nearly 70%. One of the largest hurdles to overcome in the general uptake of hydrogen fuel cells is the ability to store hydrogen fuel in a form with sufficient energy density to allow for mobile systems to be truly viable. This often means that hydrogen has to be stored at very high pressure (around 70 MPa) in bulky tanks to provide sufficient capacity. Clearly this is not suitable for smaller vehicles or portable systems. Partly to address this, there has been considerable interest in direct oxidation liquid fuelled cells due to the very high specific energy density of liquid fuels. A very compact variant of the liquid fuelled cell which has received little attention is the alkaline dissolved fuel cell where the fuel is dissolved in the electrolyte and the system relies on a selective cathode for efficient operation.

Borohydrides present a particularly good option for an alkaline dissolved fuel system, having high energy densities, a low standard potential for the oxidation to borax (an 8 electron process) and good stability in alkaline conditions. A key area in the success of a fuel cell utilizing borohydride is the development of an anode which can make use of the full 8 electron oxidation to borax directly oxidising the borohydride with as little of the hydrolysis reaction occurring as possible. This is in addition to common requirements of high activity, high stability, good electronic conductivity and transport of reactants and products. Here we present investigations into the oxidation of borohydride in alkaline media under various conditions for a selection of candidate materials in different forms using an RDE (rotating disc electrode) based procedure. Results demonstrate that hydrolysis or an indirect oxidation mechanism reduces the coulombic efficiency of the oxidation reaction observed for the materials investigated so far. There is also a significant difference in behaviour between candidate materials. The best performing materials from the RDE studies will be used to develop suitably active and durable functional fuel cell electrodes using scalable processes such as screen printing.

1. Introduction

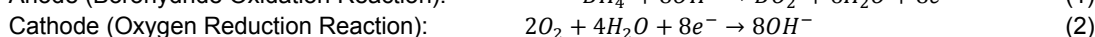
1.1 Direct Fuel Alkaline Fuel Cells

Direct fuel alkaline fuel cells (DFAFCs) are a sub-category of the alkaline fuel cell (AFC), a fuel cell which uses a hydroxide ion-based alkaline electrolyte. Whilst AFCs use hydrogen gas as their H₂ fuel source, the DFAFC utilises fuels, both organic and inorganic, which are in the liquid state and mixed with the supporting electrolyte. These liquid fuels are hydrogen-containing molecules which, used with an appropriate catalyst, can be oxidised in the anode reaction. With this come benefits such as improved operational logistics, increased safety and the potential for fuels with high energy densities sourced from green/renewable sources. At the cell level, the anode no longer requires a gas diffusion layer as the fuel diffuses from the electrolyte through to the wet pores of the anode, contrary to that of AFCs whereby the hydrogen gas diffuses through the anode to the electrocatalyst-electrolyte interface. The logistics of refuelling the fuel cell could be simplified with the addition of fresh liquid fuel compared to refilling cylinders. However, some challenges need to be addressed before the technology is commercially viable.

Along with the limitations encountered by all AFCs such as carbon dioxide contamination of the electrolyte, DFAFC also require the identification of the most appropriate fuel type from a selection of alcohols and inorganic salts, each with their own advantages and disadvantages. The presence of the cathode in high concentration fuel also requires it to be selective to the oxygen reduction reaction (ORR) such as in Equation 2).

1.2 Sodium Borohydride

Sodium borohydride, NaBH_4 , is an inorganic material which is a well-known reducing agent. In recent years it has been used as a hydrogen storage material as it can be easily hydrolysed to release the four hydrogen atoms. It can also be used as a fuel for direct borohydride membrane based fuel cells (DBFC).



NaBH_4 has a high energy density of 9000 W.h.kg^{-1} making it attractive compared to other fuels such as methanol and ethanol with 6100 and 8030 W.h.kg^{-1} respectively (Yu et al., 2012). However borohydride oxidation (BOR in Equation 1) is not a simple process. Borohydride oxidation may proceed via either: (i) hydrolysis followed by oxidation (indirect oxidation) or (ii) direct oxidation (see Figure 1). The former is less efficient because the hydrolysis reaction is exothermic, leading to a loss of energy from the system, while the latter utilises the full 1.24V to release all 8 electrons and is therefore the preferred mechanism.

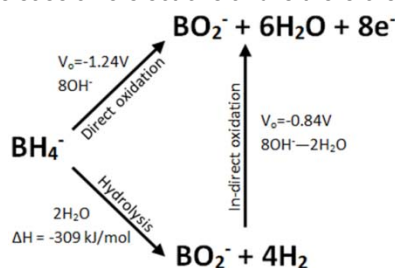


Figure 1: Oxidation of borohydride (Rostamikia and Janik, 2010).

NaBH_4 will hydrolyse in neutral to low pH's and so a highly alkaline electrolyte is desirable in order to prevent this (Davis and Swain, 1960). Since borohydride is currently being extensively researched as a hydrogen storage material, there have been studies on the reprocessing of borax, the by-product oxidation reaction to regenerate borohydride (Sanli et al., 2010). This provides the opportunity to make the fuel even more attractive for commercial use on a large scale. DBFC are a promising technology if an effective electrocatalyst can be found for its direct BOR at the anode and a cathode with a high ORR selectivity can be developed.

1.3 Electrocatalysts

Electrocatalysts are arguably the driving force of the fuel cell. The use of an unoptimised electrocatalyst can result in low efficiencies due to poor fuel utilisation, high polarisation losses or electrocatalyst degradation. Pt has been historically used as an electrocatalyst as it has been considered one of the most catalytically active material available with high kinetics for ORR and hydrogen oxidation reaction, HOR (Steele and Heinzl, 2001). However, due to its high cost and ability to be poisoned by organic fuel by-products, it has proven difficult to fully commercialise the technology (Lamy et al., 2002). Various methods have been employed to increase the surface area of Pt, therefore decreasing the amount of material required to help drive down costs. Usually this is achieved through cheap conductive carbon supports such as high surface area carbon blacks. Furthermore, the development of carbon monoxide tolerant Pt-composites in recent years have helped increased the stability of Pt as a plausible electrocatalyst (Fu et al., 2012). In this paper, Pt has been used as a model anode catalyst because of the reported fast kinetics of borohydride oxidation on Pt, although achieving full efficiency is hindered by the predominance of the indirect mechanism. Nevertheless it provides a useful baseline in this study which seeks to develop a cheaper alternative that has equal or greater activity. To this end, non-precious metal alternatives have been investigated extensively. Out of these Ni has received attention as an electrocatalyst for the oxidation of a variety of fuels. Ni has been evaluated both on its own as well as in varied alloys, such as with Sn and Cu with some success (McLean et al., 2002). Little investigation has been conducted into the use of nano Ni (nNi) as an anode electrocatalyst for the electrooxidation of NaBH_4 in a DBFC. Here we present the initial findings of use of nNi powders compared to a model Pt baseline.

2. Experimentation

2.1 Electrode Preparation

The electrocatalyst, Pt on C (Pt/C) (50 %wt Pt on Vulcan XC72R from BASF) and nNi (Ni powder 40-60 nm from Skyspring), was prepared in a suspension along with isopropyl alcohol (IPA) (Sigma-Aldrich) and Nafion® (5%wt solution from Sigma-Aldrich). The electrocatalyst (0.5 g) was initially dispensed into a glass vial followed by the IPA (10 g). This was sonicated for 5 mins to produce the suspension. Once complete the Nafion® (1 g) was added and sonicated for a further 5 mins. A preliminary investigation showed that 0.5 g was approximately the largest amount of electrocatalyst that could be held in a suspension for a workable amount of time, in 10 g IPA and 1 g Nafion®. It should be noted that the Pt/C stayed suspended in the solution for far longer, (hours), compared to the nNi, (seconds).

In order to evaluate the electrocatalysts, voltammetric techniques were used. These were conducted primarily on a RRDE (Pine E7R9 with a glassy C disc and 99.99% Pt ring) with a disc and ring geometric area (A_{geo}) of 0.2475 cm² and 0.1866 cm² respectively. An aliquot of the suspension (5 μ L) was pipetted onto the disc centre of an inverted rotator (Pine AFMSRCE) with the RRDE attached and spin coated for 15 mins (at 500 rpm for nNi and approx. 900 rpm for Pt/C). This produced a close to a uniform layer of electrocatalyst on the surface of the electrode. Before each coating RRDE was washed with DI water (18.2m Ω .cm at 25°C, Millipore Direct-Q UV 3), polished with 0.05 μ m alumina polishing solution and sonicated for 1 min after use to remove any polishing debris.

2.2 Voltammetry

Voltammetry was employed to evaluate the electrocatalyst's ability to oxidise NaBH₄, either directly or indirectly. For the voltammetry measurements a saturated calomel electrode (SCE, Scientific Laboratory Supplies) and high purity Pt wire (Sigma-Aldrich) electrode sealed into a borosilicate glass tube were used for the reference and counter electrodes, respectively.

Electrochemical analyses were conducted in a 150 mL glass cell (Pine AKCELL3) with the prepared RRDEs mounted to a rotator (Pine AFMSRCE). A high sensitivity potentiostat (Ivium CompactStat) was used for the voltammetry measurements. The electrolytes used were concentrated (3 M) KOH (Sigma Aldrich). As the electrocatalyst hydrolyses the NaBH₄, hydrogen gas is produced which becomes lodged on the surface of the electrode and can prevent transport of species to the electrocatalyst adversely affecting the results. High rotation rates are favoured to help dislodge the bubbles into the bulk electrolyte.

2.3 Pt Surface Area Measurement

The effect of BOR on a Pt electrode was investigated as preliminary experiments had indicated that the current being generated decreased with each scan. This required the active surface area of Pt/C to be measured electrochemically using cyclic voltammetry before and after a series of scans to identify any decrease in active surface area. The electrode was prepared as above (section 2.1), submerged in 0.5 M H₂SO₄ and a cyclic voltammogram was recorded at 50 mV s⁻¹. Figure 3a shows a typical result. Each peak in the voltammogram correlates to a hydrogen interaction. The peaks of interest (in the potential range -0.5 to 0.5 V (SCE) in Figure 3a) correlate to the H₂ adsorption and subsequent oxidation on the platinum surface. The active surface area of the electrode may be calculated from the charge passed from the H₂ adsorption process, which itself may be determined by a simple integration of the current-time curve (assuming a monolayer of H_{2(ads)} gives a charge passed of 210 μ C cm⁻² (Sheppard et al., 1998)).

3. Results

3.1 Borohydride Oxidation on Pt

A Pt electrode with a 0.5 g Pt/C loading was prepared and analysed in 10 mM NaBH₄/3 M KOH at a range of rotation speeds to determine the effect of mass transport (Figure 2b). The currents produced are shown in Table 1. According to the Levich equation, doubling the rotational speed increases the current produced by a factor of $\sqrt{2}$ if the current is limited by the mass transport. Rearranging the Levich equation allows for the calculation of the number of electrons being transferred during that specific electrochemical reaction. This is important as calculating n allows the amount of fuel that's being utilised to be estimated. The BOR is an 8 electron process and therefore, for example, a current that is the result of 6 electrons could be considered to utilise 75% of the borohydride fuel (assuming that the borohydride is the only fuel source). However, it must be noted that this does not take into consideration whether the electrocatalyst is selective to the direct or in-direct oxidation mechanism, only that the fuel is being consumed.

Pt is known for being a good catalyst for the BOR of borohydride, though is unspecific to direct and indirect oxidation. Analysis was conducted on the Pt ring of the RRDE and high surface area Pt/C (Figure 2a and 2b). The rationale behind conducting analysis of BOR on the Pt ring was that the current being generated would be due to the Pt alone rather than any powder preparation. This was then compared to a prepared high surface area Pt/C electrode.

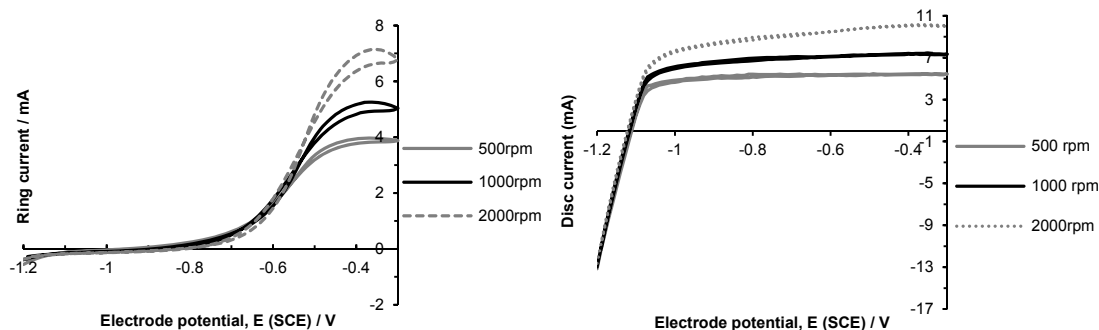


Figure 2a (left): Cyclic voltammetry of Pt ring of RRDE in 10 mM NaBH₄ + 3 M KOH, scan rate 5 mV s⁻¹, room temperature. Figure 2b (right): Cyclic voltammetry of Pt/C on vitreous carbon disc of RRDE in 10 mM NaBH₄ + 3 M KOH, scan rate 5 mV s⁻¹, room temperature

Table 1: Comparison of current and *n* values of Pt ring and Pt/C at limiting current.

Pt	Rotation Speed, <i>f</i> (rpm)	Current, <i>I</i> (mA)	Current Density, <i>j_i</i> (mA.cm ⁻²)	Charge Transfer, <i>n</i>
Pt Ring at -0.36 V(SCE) (A _{geo} = 0.1866 cm ²)	500	3.97	21.2	2.7
	1000	5.26	30.1	2.5
	2000	7.15	42.5	2.4
Pt/C at -0.3 V (SCE) (A _{geo} = 0.2475 cm ²)	500	5.44	22.0	2.8
	1000	7.34	29.7	2.6
	2000	10.0	41.0	2.5

It was expected that high limiting currents and *n* values would be observed when using the Pt however this was not the case as shown in Figure 2a and Figure 2b along with Table 1. Conducting the experiment under different rotation rates generated a steady increase in current plateau with rotational speed, which correlates with the Levich equation. This indicates that the current is mass transport limited and was largely due to the oxidation of the NaBH₄ in the solution. It was found that using a high surface area Pt electrocatalyst, i.e. Pt/C, increase kinetics as well as generate about the same transport limited current densities. The increased kinetics of the Pt/C is demonstrated by the steep gradient in Figure 2b at E < -1.0 V (SCE) compared to the gradual gradient in Figure 2a at E < -0.6 V (SCE). It has been reported that the coulombic efficiency decreases as a result of the hydrolysis reaction and so could be the reason why poor currents and *n* values were obtained (Šljukić et al., 2013). The Pt ring has a slightly lower average *n* value of 2.5 compared to the Pt/C with 2.6. This is possibly due to hydrogen bubbles being generated as a result of the hydrolysis reaction being caught on the rough surface of the Pt/C, allowing it to be further oxidised. In the case of the Pt ring the hydrogen bubbles will flow off the relatively smooth surface and out of the electrolyte.

3.2 Effect of Borohydride Oxidation on Pt/C Active Surface Area

During a current degradation experiment, to determine to what extent the limiting current being generated by a Pt/C is decreasing over cyclic scans, it was noted that there was a significant decrease in limiting current over 25 scans (-1.115 to -0.3 V (SCE)). This could be due to an alternative reaction occurring on the surface of the electrode, generating unexpected limiting currents. An experiment to understand the effect of scan number on Pt active surface area (A_{act}) was developed. A Pt/C electrode was prepared on the disc of the RRDE with the A_{act} being measured via voltammetry. This was followed by a series of voltammograms with the A_{act} being measured again at the end. The results, as seen in Figures 3a and 3b,

show a decrease in A_{act} by approx. 20%. It was hypothesised that one possibility was that BOR intermediates or products were being adsorbed onto the Pt electrocatalyst and inhibiting it. Another possibility was that the large potential range used was degrading the electrocatalyst.

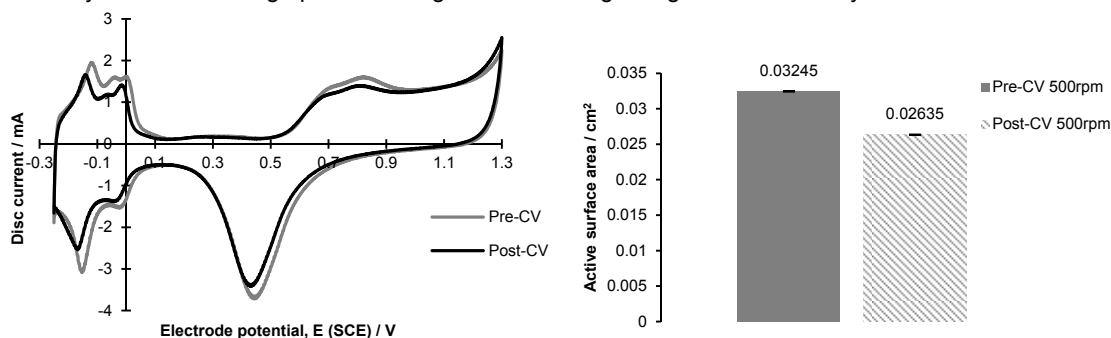


Figure 3a (left): Cyclic voltammetry of Pt/C in 0.5 M H_2SO_4 at 500 rpm rotation rate, 50 mV s^{-1} scan rate and room temperature. Figure 3b (right): Comparison of active surface area measurement of Pt/C before and after voltammograms.

This interpretation was supported by a set of experiments conducted with increasing potential range showing that as the range increased so did the rate of current degradation. The experiment did not however indicate the mechanism which causes this and further surface analysis on the electrode would need to be done in order to determine whether BOR intermediates/products were the cause.

3.3 Borohydride Oxidation on nNi

Electrochemical analysis on nNi electrode was conducted in 10 mM $\text{NaBH}_4/3 \text{ M KOH}$ to determine its fuel utilisation ability. Figures 4a and 4b show some of the preliminary cyclic voltammograms.

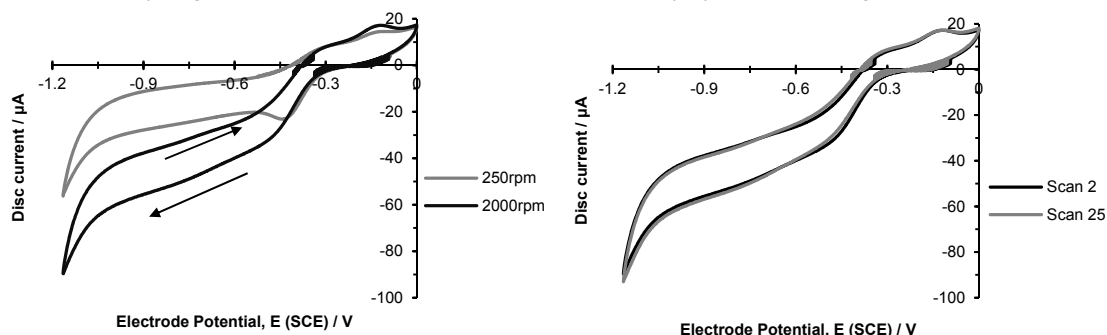


Figure 4a (left): Cyclic voltammogram of nNi in 10 mM NaBH_4 with 3 M KOH, scan rate 20 mV s^{-1} and room temperature. Figure 4b (right): Cyclic voltammogram showing current deterioration from scan 2 to scan 25, scan rate 20 mV s^{-1} and room temperature.

The first characteristic identified in the voltammograms is that the current being generated was about 2 orders of magnitude greater than the Pt based electrodes shown in Figure 2a and Figure 2b. The currents obtained in the region of the reversible potential for borohydride oxidation are also indicating the reduction of a species as opposed to the oxidation which would have been expected. The small oxidation currents at ca. -0.5 to 0 V (SCE) is not apparent in any of the Pt results. Several voltammograms at different rotation rates were completed to establish the effect of mass transport on the current being generated (Figure 4a). The oxidation waves do not shift but the species being reduced at $E = < -0.5 \text{ V}$ (SCE) does, indicating that whatever is being reduced must be in solution. The effect of scan number on current degradation was investigated by comparing the voltammograms produced at scan 2 and scan 25 (Figure 4b). There is little discernable change across the potential range. A cyclic voltammogram of nNi in 3 M KOH electrolyte only was compared to Figure 4b showing that the two systems responded with very similar characteristics. It is therefore likely that the currents observed are associated merely with growth and reduction of a surface Ni hydroxide species and the reduction of dissolved oxygen in the electrolyte. The measured dissolved oxygen concentration was, 4.5 mg L^{-1} (Milwaukee MW 600 DO meter), which is around a third of what

would be expected when the approximate transport limited current density is calculated according to Levich equation.

4. Conclusions

4.1 Platinum Electrocatalyst

As expected Pt has been shown to have the potential to be an effective oxidation catalyst for borohydride. It has been confirmed as having fast kinetics and the effect of using a high surface area supported catalyst as shown by the Pt/C is marked and could produce an effective anode catalyst. However, Pt has two significant technical disadvantages. The first is its unselective oxidation mechanism, and therefore lower than ideal efficiencies with the second being the generation of problematic hydrogen bubbles by hydrolysis reducing the fuel utilisation efficiency. Finally the cost of Pt could make it difficult to be commercially viable.

4.2 Nano Nickel Electrocatalyst

Taking the data presented in this paper, the particular nNi explored does not appear to be suitable for BOR. The currents generated are very low and most likely being generated by the presence of dissolved oxygen in the electrolyte and the oxidation / reduction of the nNi surface itself. Ni is known for having low fuel efficiencies for BOR at approx. 50% but the low cost of Ni, when compared to the generally highly active noble precious metals, still makes it an intriguing, possibly viable choice that could be exploited (Ma et al., 2010).

Acknowledgements

The work presented was financially supported by the Engineering and Physical Sciences Research Council (EPSRC) and AFC Energy Plc.

References

- Davis, R. E. & Swain, C. G. 1960. General Acid Catalysis of the Hydrolysis of Sodium Borohydride^{1,2}. *J. Am. Chem. Soc.*, 82, 5949-5950.
- Fu, Z., Huang, Q. M., Xiang, X. D., Lin, Y. L., Wu, W., Hu, S. J. & Li, W. S. 2012. Mesoporous tungsten carbide-supported platinum as carbon monoxide-tolerant electrocatalyst for methanol oxidation. *Int. J. Hydrogen Energy*, 37, 4704-4709.
- Lamy, C., Lima, A., Lerhun, V., Delime, F., Coutanceau, C. & Léger, J.-M. 2002. Recent advances in the development of direct alcohol fuel cells (DAFC). *J. Power Sources*, 105, 283-296.
- Ma, J., Sahai, Y. & Buchheit, R. G. 2010. Direct borohydride fuel cell using Ni-based composite anodes. *J. Power Sources*, 195, 4709-4713.
- McLean, G. F., Niet, T., Prince-Richard, S. & Djilali, N. 2002. An assessment of alkaline fuel cell technology. *Int. J. Hydrogen Energy*, 27, 507-526.
- Rostamikia, G. & Janik, M. J. 2010. Direct borohydride oxidation: mechanism determination and design of alloy catalysts guided by density functional theory. *Energ. Environ. Sci.*, 3, 1262-1274.
- Sanli, A. E., Kayacan, İ., Uysal, B. Z. & Aksu, M. L. 2010. Recovery of borohydride from metaborate solution using a silver catalyst for application of direct rechargeable borohydride/peroxide fuel cells. *J. Power Sources*, 195, 2604-2607.
- Sheppard, S.-A., A. Campbell, S., R. Smith, J., W. Lloyd, G., C. Walsh, F. & R. Ralph, T. 1998. Electrochemical and microscopic characterisation of platinum-coated perfluorosulfonic acid (Nafion 117) materials[dagger]. *Analyst*, 123, 1923-1929.
- Šljukić, B., Milikić, J., Santos, D. M. F. & Sequeira, C. a. C. 2013. Carbon-supported Pt_{0.75}M_{0.25} (M = Ni or Co) electrocatalysts for borohydride oxidation. *Electrochim. Acta*, 107, 577-583.
- Steele, B. C. H. & Heinzel, A. 2001. Materials for fuel-cell technologies. *Nature*, 414, 7.
- Yu, E. H., Wang, X., Krewer, U., Li, L. & Scott, K. 2012. Direct oxidation alkaline fuel cells: from materials to systems. *Energ. Environ. Sci.*, 5, 5668-5680.