Plasma Electrochemistry: Development of a Reference Electrode Material for High Temperature Plasma

Toks Fowowe, Emina Hadzifejzovic, Jingping Hu, John S. Foord, and Daren J. Caruana*

Electrochemical science underpins an enormous array of technologies ranging from sensors and power sources to coating and metal smelting. Much of this progress was possible due to the invention of the reference electrode,[1] which has enabled a profound understanding of redox reactions at solid surfaces in liquids. In contrast, the corresponding reactions at the solid/gas interface still remain unexplored. The development of a reference electrode which is functional in the gas phase will extend and further facilitate the early work in the area of dynamic electrochemistry in gaseous plasmas.[2] We describe the assessment of a unique reference electrode capable of establishing a redox potential through its innate chemical make-up. Several materials are tested, composed of mixtures of powdered metal and corresponding metal oxide species which serve to maintain a potential at the interface between a solid and a gaseous plasma.[3]

There are few examples using plasmas as media where electrochemical processes are investigated. Richmonds and Janek investigated the charge transfer processes at the plasmaliquid interface.[4] More relevant to this work, Janek and Ogumi,[5] described the use of non-thermal plasma for metal surface oxidation. Our work has focused entirely on flame plasmas, which are considered as electrolys, their negative species being predominantly free electrons and their positive species being molecular or atomic cations.[6] For the purposes of this work the ions produced by combustion reactions in flames make up the background electrolyte, they serve no other role except to provide a conducting medium between two electrodes.[4,4a,4b,5a] We have previously reported the construction of two compartment flame electrochemical cells containing polarizable electrodes to enable measurement of potential difference.[7] Here we confine the potential determining material in the solid state to produce a self-contained reference electrode, rather like a metal/insoluble metal salt (e.g., silver/silver chloride) reference electrode, but in this case we have used metal powder and the corresponding metal oxide. We associate the measured potential difference (PD) to composition and candidate potential determining redox processes with support from ex situ analysis of the reference electrode material. The stability of the potential and the extent of non-polarisability were assessed using chropopotentiometry with and without applied current.

All reference electrodes constructed in this work were composed of a powdered mixture containing a metal and its complementary metal oxide, packed into a recrystallized alumina ceramic tube. A length of nickel-chromium wire was used to make electrical connection with the reference electrode material. The PD was measured between a high surface area graphite rod pseudoreference electrode and the reference electrode using a high input impedance electrometer. The PD recorded for 5 different metal/metal oxide materials are shown in Table 1. It is clear that potential for each electrode with metal/metal oxide mixtures was defined by the identity of the metal. The issue with the difference in behaviour of the different electrodes was the PD stability with time. For most of the electrodes the PD drifts over a period of 2000 seconds, in some cases >200 mV and stabilises towards the end of this time. In some cases the drift was due to loss of material from the ceramic tube, particularly for Zn/ZnO and Mo/MoO3.

The measured PD for the five metal/metal oxide materials given in Table 1 were correlated to the calculated potential from Gibbs energies of formation of the components according to the reaction Mz(s) + xO2(s) = MOx(s).[8] The correlation is very good for all but the Mo and Zn systems, as expected due to the evaporation/sublimation discussed above (Figure 1). These measurements assume that the carbon pseudoreference electrode provided a stable potential difference and any drift was small compared to the drift observed for the metal/metal oxide reference electrodes.

The main objective of this work was to construct a non-polarisable interface, exhibit a stable potential and above all to understand how these electrodes and materials behave in a flame plasma environment. Polarisation curves, when an external current is passed through the electrode whilst recording the PD, are good diagnostic tools to assess the extent of polarisability of the reference electrode material. The most stable metal/metal oxide mixture was found to be the Ti/TiO2 mixture electrodes stabilised after the first 400 seconds. For this reason Ti/TiO2 mixtures were chosen for further study. Figure 2 shows the polarisation curves for a number of electrodes constructed with a number of different Ti/TiO2 mixtures. For comparison a platinum disc in a ceramic tube was also used as a reference electrode (with the same geometric surface area as the Ti/TiO2 reference electrodes) to provide a point of comparison for a polarisable surface. In contrast, reference electrode containing mixtures of Ti/TiO2 had more linear and steeper polarisation responses, indicative of a non-polarisable interface, i.e. excellent reference electrode behaviour. There was also a clear trend of the PD on the composition at zero current; as the amount of metal powder was increased the potential was

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shifted more negative at zero current. Also the gradient of the polarisation curves is dependent on the composition with a trend Ti/TiO$_2$ > 20/80 Ti/TiO$_2$ > 50/50 Ti/TiO$_2$ > 80/20 Ti powder. Whereas, the platinum disc and Ti powder electrodes show typical polarisation characteristics as expected for metallic materials in contact with an electrolyte medium. The polarisation response of the conducting materials show typical conductivity characteristics seen at a two electrode Langmuir probe in plasma, as expected.\[6a,9\]

The long-term behaviour of these electrodes was of particular interest and so understanding the chemical and physical changes of the reference electrode material after it has been exposed to the flame. In addition it was clear that Ti and TiO$_2$ seem to withstand the physical conditions of the flame, i.e. high temperature and chemical reactivity. Two contrasting ratios, 20/80 Ti/TiO$_2$ and 80/20 Ti/TiO$_2$ were investigated. Polarisation scans over a current range between $10^{-7}$ to $10^{-7}$ A, are shown in Figure 3. The potentials for both electrodes were in the same range, and over the course of 10 scans the change in potential of approx. 140 mV was observed. The change in potential between the first and tenth scan occurred at different points. For the 20/80 electrode the change occurred during the eighth scan, 560 s. In contrast the 80/20 electrode experienced this change earlier, approximately 350 s. This potential shift was linked to a change in the composition of the material in the ceramic tube. The calculated change in PD for a single electron process per decade change in concentration at 1200 K would be 103 mV, which is reasonably close to what we measure.

The composition of the reference electrodes used for the polarisation tests were analysed by sectioning the electrode tips to expose the Ti/TiO$_2$ material. The images of the exposed material and corresponding Raman profiles along the length for six different electrodes, three for each mixture which have been immersed in the flame for 70, 560 and 700 seconds, are shown in Figure 4. The following points can be drawn: (1) There is no significant loss of material, which was sintered and very stable. (2) For all the electrodes a white material that was segregated at the opening in direct contact with the flame was identified from the Raman spectral profiles as rutile TiO$_2$. (3) The rate of growth of the TiO$_2$ rich area was faster in the 20/80 Ti/TiO$_2$ material compared with the 80/20 Ti/TiO$_2$. (4) The dark material for all the 80/20 Ti/TiO$_2$ was found to be predominantly TiN as confirmed by XRD and XPS, see SI for details. For the 20/80 Ti/TiO$_2$ electrodes the dark materials was composed predominantly of Ti$_3$O$_5$ again from XRD (see SI).

It is possible to deduce a number of dynamic changes from the ex situ observations listed above, that may be correlated with the changes in the PD behaviour of the electrodes. The

![Figure 2](image-url)  
Figure 2. Current voltage polarisation curves for reference electrodes containing Ti powder (■), TiO$_2$ (●), 20%, 50%. 80% Ti (○, △, ◆) different ratios of Ti/TiO$_2$ pastes placed into ceramic tubes. A platinum disc of similar surface area as the paste was used as a reference (□). Step currents (10 s each) from $3 \times 10^{-7}$ A to $3 \times 10^{-7}$ A were passed through the electrode and voltage recorded vs. graphite electrode.

### Table 1. Potential difference for reference electrodes made with different metal/metal oxide materials packed in a ceramic tube support. All reference electrode materials were 50/50 by weight and PD was measured against a carbon rod pseudoreference electrode, with the exception of graphite which was a graphite rod of identical dimensions as the pseudoreference electrode. The voltage was recorded for 2000 s and the potential difference presented is the average and the standard deviation for the voltage between 1500 and 2000 s.

<table>
<thead>
<tr>
<th>Material</th>
<th>Potential difference/V vs. Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/CuO</td>
<td>0.58 ± 0.07</td>
</tr>
<tr>
<td>Fe/Fe$_2$O$_3$</td>
<td>1.14 ± 0.07</td>
</tr>
<tr>
<td>Mo/MoO$_3$</td>
<td>1.35 ± 0.15</td>
</tr>
<tr>
<td>Nb/NbO$_2$</td>
<td>0.90 ± 0.06</td>
</tr>
<tr>
<td>Ti/TiO$_2$</td>
<td>0.65 ± 0.07</td>
</tr>
<tr>
<td>Zn/ZnO</td>
<td>2.27 ± 0.20</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.0 ± 0.03</td>
</tr>
</tbody>
</table>

![Figure 1](image-url)  
Figure 1. Correlation of the experimentally measured PD $E_{(expt)}$ with calculated PD $E_{(calc)}$ for the 6 different metal/metal oxide reference materials. $E_{(calc)}$ determined using thermodynamic data from ref [8].
Figure 3. Showing the current/voltage polarisation curves for 20/80 (a) and 80/20 (b) Ti/TiO₂ electrode. Ten scans were collected with the 2nd (●), 4th (■), 6th (○), 8th (▲) and 10th (▼) shown. Each point represents an average PD vs. graphite electrode for ten second, for seven current values between the range +1 × 10⁻⁶ to −1 × 10⁻⁸ A.

The expanding TiO₂ section was probably due to the conversion of TiO₂ to the opening exposed to the flame was very prevalent and very rapid (clear after 70 s), suggesting a degree of mobility of oxygen through the solid reference electrode material at high temperatures. The difference in the thickness of the TiO₂ layer at 70 s showed slight dependence on the original mole fraction of TiO₂ for the two electrode mixtures. For the 80/20 Ti/TiO₂ electrodes, the initial mole fraction of TiO₂ was 0.142, most of which seemed to segregate at the flame interface with the rest of the material almost devoid of oxide. Whereas for the 20/80 Ti/TiO₂ reference electrode, (with an initial TiO₂ mole fraction of 0.705) the oxygen species seems to be partitioned between the outer flame interface and the rest of the dark material in the form of Ti₃O₅. Beyond 70 s the oxide section grows at a fast rate in the oxide rich electrode, 20/80 Ti/TiO₂, until there is a total conversion to TiO₂ throughout the material.[10] Clearly rutile phase increases in conjunction with the decreasing Ti₃O₅ phase, from this we suggest that Ti₃O₅ is oxidised into TiO₂, perhaps via an oxinitride intermediate, which was also identified in the material by XRD and XPS (see SI).[11]

The growth of the TiO₂ phase was far slower for the 80/20 Ti/TiO₂, which reaches approx. 40% of the total material after 700 s. The conversion of Ti metal to TiN was not surprising in this environment, which was probably aided by the large solubility titanium exhibits for nitrogen at high temperatures.[12] The expanding TiO₂ section was probably due to the conversion of TiN in the presence of oxygen, probably proceeding through the solid-gas reaction TiN + O₂ → TiO₂ + ½N₂.[11,13] The oxide region on the non-flame end of the reference electrode pellet is the natural growth of TiO₂ due to oxygen diffusion from the ambient air.

In the context of this work, it is important to rationalise the physical origin of the potential difference measured. As demonstrated by the construction of two mixtures of Ti/TiO₂ materials, the potential difference relative to the graphite pseudo reference electrode was not very different; within experimental error. This implies that the potential defining processes are also quite similar, supporting the discussion above that the identity of the metal/metal oxide mixture is the potential determining process. Compositional changes are within the reference electrode material over the period of 700 s, probably correspond to the changes observed in the potential difference shown in Figure 3.

As titanium was present in more than two oxidation states the potential difference was almost certainly a mixed potential process. However, it should be stressed that all the characterisation described here were all performed ex situ, the potential defining processes may be linked to species(s) that are inherently unstable. One such species is oxygen; as TiO₂ is known to be a good oxygen ion conductor at high temperatures.[14] Undoubtedly, oxygen species are able to diffuse through the reference electrode material. The presence of O₂ in the flame and O₂⁻ in the reference electrode material may establish a potential difference at the gaseous interface. The density of oxygen ions expressed as activity, aO₂⁻ = γ[O₂⁻]/[O₂]₀ in the solid state, which may be related to the potential difference, E₉₀⁻→O₂⁻, at the interface between the reference electrode material and the flame medium, through the Nernst equation:[13]

\[
E_{O_2^->O_2^=} = E_0^{O_2^->O_2^=} - \frac{RT}{2F} \ln \left( \frac{a_{O_2^-}}{a_{O_2^2}} \right)
\]  

(1)

Where \( E_{O_2^->O_2^=} \) is the potential difference under standard conditions, \( a_{O_2^-} \) is the activity of molecular oxygen in the flame, R, T and F have their normal meanings. The change in PD with time versus graphite was probably due to the change in \( a_{O_2^-} \) in the reference electrode material, due to changes in composition altering the oxygen vacancies sites, as given by equation (1). It is likely that the potential difference is a combination of these processes, and others (involving nitrogen ions[16]) leading to a mixed potential. The electrode was reasonably static with very little deterioration of the material. This along with the long-term stability appears to be suitable for use as a reference electrode.

In summary, a conveniently constructed reference electrode has been described which can be used for electrochemical measurements in flame plasma. The potential difference measured was dependent on the identity of the metal species used. Titanium/titanium oxide mixtures offer very good qualities as flame plasma reference electrode material due to their low level of evaporation (or sublimation) and stability of the PD, which develops at the Ti/TiO₂ flame interface. The potential defining process was probably a combination of the disproportionation of the Ti and O₂(gas)/O₂⁻ (solid) redox processes. Work of this nature extends the utility of electrochemistry in plasma, beyond
conductivity probes for the development of new plasma diagnostic tools.\[17\] A reference electrode would enable quantitative gas phase voltammetry, complementing analytical techniques such as atomic absorption, inductively coupled plasma and fluorescence spectroscopies. In addition, it is possible that substantial impact on other less well established fields where solid/gas surface redox reactions may also be anticipated, such as electrostatic charging,\[18\] catalysis\[19\] and astrochemistry.\[20\]

Experimental Section

A Méker type burner was used throughout this study, which supports a flame fed by a premixed hydrogen, oxygen and nitrogen with the desired relative flow rates, shown in Figure S1.\[7a\] Caution: Explosive gas mixture, adequate safety precautions should be taken. An electrically insulating burner top (MACOR®) was essential for this work because a conducting burner top would actually bridge the flames together and cause erroneous measurements and drift. Reference electrodes were freshly made just before use by mixing thoroughly a mixture of metal and the corresponding metal oxide powders with the appropriate weight% to make paste with methanol, and packed in the end of a ceramic tube to a depth of 3–4 mm. A length of 0.5 mm diameter piece of nickel-chromium (Kanthal Ltd., UK) wire was used to make electrical contact with the paste. The ceramic reference electrode and a graphite rod of same dimensions were positioned opposite one another centrally in the flame at 10 mm above the burner and 5 mm apart from each other, using two \(x\), \(y\) and \(z\) micropositioner platforms with the horizontal axis of each platform motorized (PI, supplied by Lambda scientific, UK) and controlled remotely by a computer. The zero current potential difference between the two electrodes was measured using a data acquisition card (NI USB-6215, National Instruments) with input impedance above 10 GΩ. A NI LabVIEW Signal Express LE interactive software (National Instruments) was used to log the data. Other electrochemical measurements were performed using a potentiostat (Autolab PGSTAT 100, Eco Chemie B.V. supplied by Windsor Scientific Ltd., UK) with 100 V compliance voltage.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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