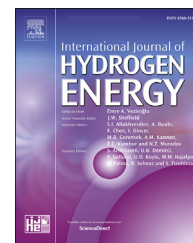




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Short Communication

Electrocatalytic hydrogen evolution using metal-free porphyrins

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ABSTRACT

The direct deposition of metal-free porphyrins onto carbon electrodes to conveniently form hydrogen production cathodes is reported for the first time. It is revealed that the rate of hydrogen generation can be optimised by adding appropriate substituents to the tetraphenyl-porphyrin (TPP) molecule, with electron donating groups enhancing performance. Excellent electrocatalytic behaviour is evident with a Faradaic efficiency of about 90%. Turn over numbers (TON) of up to 100,000 for TPP and 250,000 for Methoxy-TPP are observed after 1 h of electrolysis. These electrodes are stable for at least 6 h and can be re-used several times without reducing the TONs and Faradaic efficiency. The influence of substituents is discussed in terms of a scenario where the discharge of a hydronium ion by a ring nitrogen atom is apparently rate determining. This work reveals that metal-free macrocycles can be tuned to promote electrochemical water splitting, with the potential to offer cost-effective and sustainable alternatives to precious metal based electrocatalysts.

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Introduction

With increasing CO₂ levels in the atmosphere, novel environmentally friendly energy conversion and storage devices are required to alleviate climate change. Accordingly, interest in the development of H₂ as a storable and carbon neutral energy carrier has intensified. However at present, the dominant method of hydrogen production, steam reforming, relies on fossil fuels and therefore is not carbon neutral [1–3]. By contrast electrocatalytic H₂ production via water electrolysis does not involve CO₂ emission if driven by renewable

electricity [4,5]. Platinum is the most commonly employed catalyst owing to its low overpotential and high efficiency for the hydrogen evolution reaction (HER), however, its cost has inhibited the widespread adoption of electrochemical water splitting [6–8]. While non-precious transition metals [9], their alloys [10,11] and composites [12] have been utilised as HER electrocatalysts in alkaline media [13], these are not suitable for application at lower pH (as in proton exchange membrane electrolyzers) due to their rapid corrosion [14,15]. In view of this, attention has been devoted to the development of compound catalytic materials such as metal chalcogenides [16,17], carbides [18,19] and phosphides [20,21], but stability issues

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persist [22]. Such materials are typically supported on conductive carbon electrodes, although it is worth noting that carbon itself possesses poor activity for the HER [23].

An alternative approach involves the use of *molecular electrocatalysts* which can also be immobilised on carbon. In this regard, a number of groups have recently studied metallated porphyrins [24,25] and phthalocyanines [26,27], and have shown that these metallated macrocycles produce hydrogen at relatively positive potentials [28–32]. In contrast, the metal free analogues have received little attention. One report in the literature used free-base porphyrins for electrocatalytic CO₂ reduction, and under these conditions observed hydrogen evolution [33]. More recently, metalloporphyrin frameworks have been reported to result in enhanced selectivity of CO₂ electroreduction [34,35]. The only publication that we are aware of that is similar to the results presented here, is a very recent publication by Bhaumik and co-workers who reported that metal-free covalent organic polymers containing aminoporphyrins are active for hydrogen evolution, at low overpotentials with TONs of 1328 for hydrogen generation [36]. However, to the best of our knowledge, the catalytic activity of electrodes coated with thin layers of metal-free porphyrins for hydrogen production has not been reported.

In the present work, we report an assessment of the electrocatalytic hydrogen generation capacity of carbon electrodes modified with four metal-free porphyrins: TPP, MeOTPP, BrTPP and MPyTPP (Fig. 1). The performance and stability of the four compounds were optimised by a systematic variation of the main operational parameters such as: pH, agitation, temperature and the use of a light source. The most promising results were obtained for TPP and MeOTPP analogues, which, after one hour of bulk electrolysis produced turnover numbers (TONs) of 100,000 and 250,000 respectively.

Materials and methods

The porphyrins were synthesised (see [Supplementary Info, S1](#)) using literature methods [37]. All electrochemical experiments were conducted using a CH Instruments CHI600a potentiostat. Characterisation of the redox chemistry of the porphyrins (as 1 mM solutions with 0.1 M TBAPF₆ in DMF) was

carried out in a V shaped cell ([Supplementary, Fig. S5](#)) with a glassy carbon working electrode (CH Instruments, 0.07 cm²), a platinum wire counter electrode, and a Ag/Ag⁺ reference electrode filled with 0.1 M TBAPF₆ in CH₃CN – see [Supplementary, S3](#) for full details.

For the H₂ generation studies (cyclic voltammetry and bulk electrolysis) the same type of glassy carbon electrodes were modified by drop casting 1.5 μL volumes of 0.1 mM porphyrin catalyst solutions (in DMF), prior to drying overnight. Aqueous buffer solutions were used as electrolyte, with an Ag/AgCl (3M KCl) reference electrode and a platinum mesh counter electrode. Split H-cells ([Supplementary, Fig. S6](#)) were used in these experiments, to avoid interference of oxygen generated at the counter electrode with the hydrogen generating reaction [38]. Values of current density *j* are quoted with respect to the geometric area of the electrode. The amount of H₂ produced by the bulk electrolysis was quantified by gas chromatography. For further details see [Supplementary, S4](#). TONs were based on the assumption that all material deposited was electroactive and their method of calculation is detailed in [Supplementary, S5](#).

Results and discussion

Porphyrin redox characteristics

Reductive electrochemistry of a porphyrin generally consists of two mono-electronic processes which result in the formation of a radical anion, [porph]·⁻ and dianion species, [porph]²⁻ [39]. Cyclic voltammograms (CVs) of the studied porphyrins in DMF solution are presented in [Figs. S7 – S10](#), with the reduction and oxidation potentials reported in [Table 1](#), where the voltage separation between anodic and cathodic peaks are shown in parentheses.

All porphyrins exhibited two mono-electronic reductions within the potential window of the solvent as expected. A third reductive process is visible for MPyTPP, BrTPP and MeOTPP. The nature of this feature is at present not clear. Oxidation processes generally consist of two mono-electronic oxidations of the porphyrin ring yielding the radical cation, [porph]·⁺ and the dication, [porph]²⁺ [40]. Only one oxidation

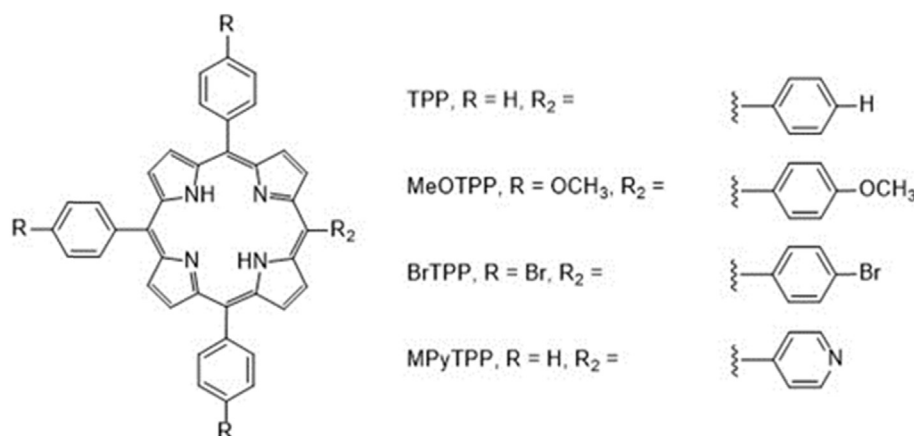


Fig. 1 – Molecular structures of TPP, MeOTPP, BrTPP and MPyTPP.

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