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A continuous in-situ EPR electrochemical reactor as a rapid in-depth mechanistic screening tool for electrocatalysis

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Abstract

In this work, an improved *in-situ* EPR hydrodynamic electrochemical cell design is constructed and validated. The created platform enables the fast and accurate screening of new electrocatalytic materials, providing insights into their effects on radical products of a reaction. Furthermore, it is essential that the reaction kinetics are not influenced by the set-up and that mass transfer can be controlled. Our modular design allows for fast and easy replacement of parts and adjustments to electrodes in order to unravel the catalysts' influence on radical formation. The proximity of the pseudo-reference electrode to the working electrode in combination with the flow and electrode positioning allows for good potential control. The POM housing allows easy manipulation of the channel and excludes the use of sealing agents.

Keywords

in-situ EPR spectroscopy, electrochemical flow cell design, channel electrode, electrochemical reduction, radical detection.

1. Introduction

Since the 1960s, the combination of Electron Paramagnetic Resonance (EPR) with electrochemistry has been established as a technique to generate, detect and identify radicals [1,2]. Numerous electrodes that can fit inside a commercial flat-cell or EPR-tube for *in-situ* radical production have been developed. These designs include electrodes constructed with laminated meshes, wires and physical vapour deposition [3,4,5]. They are easy to make and can be fairly cheap depending on the electrode requirements of the system.

Today a principal focus of the electrochemical community is the development of electrocatalysts for improving the current efficiency and stability of numerous industrial applications. A key issue for its success is a thorough understanding of the underlying mechanism of the catalytic process. To this end, EPR is a powerful tool that can detect radical

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reaction intermediates, whereas most other methods can only detect products of subsequent reactions [5,6]. Despite these benefits, it is important to stress that most modern EPR spectrometers employ resonators of restricted dimensions, which limits the amount of conducting materials that can introduced in order not to disturb the magnetic field or microwaves.

From an electrochemical perspective, the commonly used flat-cell set-ups have many drawbacks: i) the cell surfaces are mostly irreproducible, ii) the shape of the surface and the small cell size compared to the electrode surface area prevent semi-infinite linear diffusion, and iii) the potential control is done by a pseudo-reference electrode [4,5], which needs to be well-positioned for data collection to be reliable, *i.e.* adjacent to the working electrode and in a stable environment. Often in static set-ups the pseudo-reference and the working electrode are positioned in the flat section of the cell where radicals are generated using chronoamperometric techniques. However, the potential of the pseudo-reference can fluctuate during the experiment, as reactants are consumed and products are generated that subsequently diffuse from the flat section. These shifts in potential cannot be detected before or after the experiment using a known redox couple. More advanced set-ups have yielded improved sensitivity [7,8] or allow hydrodynamic characterised flow [9]. For the latter, Compton *et al.* reported a rectangular set-up where the reference and counter electrode were positioned at larger distances from the working electrode combined with the use of a current booster [10]. In another paper the effect on peak displacement was calculated [11]. Alternative geometries for hydrodynamic electrodes have been reported such as tubes, wall-jets and microchannel reactors [12,13,14,15,16].

Despite these advances, the use of EPR in combination with *in-situ* radical generation techniques remains underexploited in electrocatalyst screening. Herein we describe an *in-situ* flow-cell utilising channel electrodes made out of polyoxymethylene (POM) with the advantages of being modular, facilitating flow electrochemistry, allowing good potential control and the use of POM as a sealing agent. We have evaluated this platform using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) on p-benzoquinone (BQ) in water, and chronoamperometry coupled to continuous wave (CW) EPR at X-band on BQ in acetonitrile and methyl viologen (MV) in water.

2. Experimental

2.1 Chemicals

Acetonitrile (ACN, ≥99.9 %) is purchased from Chem-Lab. Benzoquinone (≥99.5%), methyl viologen (98%) and tetrabutylammonium perchlorate (TBAP, n-Bu4NClO4, 99.0%) are purchased from Sigma-Aldrich. Sodium sulphate (99.0%) is supplied by Acros Organics. All chemicals are used without further purification. Aqueous solutions are prepared with Milli-Q water (18.2 MΩcm). All solutions are purged with nitrogen before being pumped into the set-up.

2.2 Set-up

The constructed cell is made out of two pieces of POM (Eriks Baudoin) of which one contains a small channel with a width of 6 mm and a height of 0.4 mm. The electrodes are embedded in

the second part by melting. The working electrode is a silver foil (99.9985%) from Alfa Aesar, the counter electrode is a platinum sheet (99.95%) from Goodfellow and the pseudo-reference electrode is a platinum wire (99.99%) from Science Products. The reference is located less than 1 mm upstream of the 4 by 5 mm working electrode and the counter electrode is positioned 3.3 cm downstream of the working electrode and measures 4 by 25 mm (Figure 1). It can be further observed that between the work and counter electrode, the use of POM is minimized. From here on, this part is called 'the window'. This part is positioned in the sensitive part of the resonator where microwaves form standing waves. Connections are made with Teflon rings which are held in place with PEEK spacers.

The channel itself has a reservoir at the inlet, followed by a narrow channel of 35x2x0.4 mm which then results in the wider channel where the electrodes are positioned.

2.3 Electrochemistry

Electrochemical measurements are performed using an Autolab PGSTAT302N potentiostat without any need for a current booster. Potentials applied in the experiments are derived from CV cathodic peaks. Electodes are subsequently polished with 1µm and 0.3µm Al_2O_3 powder from Streurs.

2.4. EPR spectroscopy

The cell is positioned in a TE102 cavity in an X-band Bruker E580 Elexsys spectrometer in continuous wave (CW) mode with the working electrode positioned under the sensitive part of the resonator and the counter electrode above.

<Figure 1>

Figure 1: Exploded drawing of the *in-situ* EPR channel electrode.

3. Results & discussion

3.1 Cell design

By adapting a previously reported modular design [9], our channel flow-cell enables the easy replacement and adjustment of electrode materials and improves reproducibility of the results. Our channel configuration where the inlet to the working electrode is 40 mm ensures a Poiseuille flow profile [17] with respect to the flow rates used in this work, which allows the determination of kinetics and mass transfer parameters. Potential control is achieved by positioning the pseudo-reference less than 1 mm upstream from the working electrode in an environment where it is not affected by concentration changes or products that are formed at the counter electrode. In our set-up the potential of pseudo-reference only shifted 20 mV over 3 working hours. POM is used to build the channel flow-cell because this cheap material is rigid, easy to handle, can be milled, sealed by melting and is resistant to most solvents. It also does not give an EPR signal in the organic radical region. However, solid pieces of POM make the cavity harder to tune, reducing the sensitivity. Therefore, we have introduced the window in our design which reduces the amount of POM to 0.8 mm inside the sensitive part of the resonator. This resulted in good tune-ability of the resonator, implying that POM is suitable for use in EPR applications. The window also provides a visual detection of the formation of coloured radicals and products, when not positioned in the resonator. By sealing the setup with the same material, the use of potentially reactive sealing agents is avoided. The POM elements are easy to reproduce and precious metal components can be recovered for reuse. To the best of our knowledge this is the first *in-situ* EPR electrochemical set-up construct with POM.

3.1 Electrochemical characterisation

The two electron reduction of BQ in unbuffered water [18] was used to characterise the electrochemical properties of the cell. For more mechanistic information the reader is referred to the literature [19,20,21]. During the electrochemical characterisation, different Ag working electrodes were used in order to see the influence of the replacement of electrodes. This did not result in any changes on the measurements.

To validate if the cell fulfils the boundary conditions of a channel flow cell electrode, the diffusion coefficient of BQ is calculated by applying the following equation for channel electrodes [22]:

$$I_{l,c} = 0.925nFc^*\omega x_e^{2/3}D^{2/3}\left(\frac{v_F}{h^2 d}\right)^{1/3} \quad (1)$$

where $I_{l,c}$ is the limiting current, n is the number of electrons transferred, F is the Faraday constant, c^* is the concentration, ω and x_e are the width and length of the working electrode, D is the diffusion coefficient, v_F is the linear velocity of the solution, h is half-height of the channel and d is the width of the channel. The same order of magnitude and linearity is observed with our set-up (Figure 2), hence fulfilling the necessary conditions of a channel electrode, as was expected. D was determined to be 8.545×10^{-10} m²/s in the channel flow-cell which was very similar to the value obtained from rotating disc electrode (RDE) measurements in bulk (8.454×10^{-10} m²/s). Both of which were within the literature range for BQ and hydroquinone ($7.3\text{-}12.6\times10^{-10}$ m²/s [23,24,25]). Other than the expected increase in current, the CVs recorded

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with and without flow display some differences (Figure 2). The static CV is distorted in the sense that the oxidation peak has a more negative potential than the reduction peak. This effect could be caused by a local change in pH or a changing environment of the pseudo-reference. In flow, the reduction peak is broader and bigger than the oxidation peak. This is most likely caused by the convection of recently reduced species away from the electrode in the microchannel reactor. Hence, reversible oxidation is hindered afterwards. We want to stress out that the usage of CV has the purpose of determining the potential that should be applied for radical generation.

<Figure 2>

Figure 2: (A) LSV in the channel electrode of 5 mMBQ reduction in water with 0.2 M Na_2SO_4 at pH 4.5 recorded at 10 mV/s (B) Linearity of data compared to equation (1). (C) CV of the same solution at 0.007847 ml/s and 50 mV/s.

3.2 Spectrometric characterisation

The one electron reductions of BQ in acetonitrile [18] and of MV in water [7] are used to assess the performance of the channel flow-cell inside the resonator for *in-situ* generation and EPR detection of radicals. The applied potentials for radical generation are derived from the *in-situ* CVs (Figure 3). The obtained spectra from the chronoamperometric EPR measurements are in accordance to literature [7,14]. $BQ^{.-}$ shows a very clear spectrum after one scan which indicates that the lifetime of this radical is sufficient to reach the sensitive part of the cell in resonator before decaying. On the other hand, $MV^{.+}$ show a noisier spectrum even after 35 scans which is consistent with the relatively shorter lifetime of the radical. In *ex-situ* CV experiments at a flow rate of 0.00416 ml/min the blue colour of $MV^{.+}$ did not migrate to the most sensitive part in the window. This suggests that an substantial amount of the generated $MV^{.+}$ have already decayed before arriving at centre of the window, which coincides with the centre of the resonator where its sensitivity is maximized. It should be noted that water is not an ideal solvent because its polarity affects the magnetic field. The use of higher flow rates and higher microwave power only resulted in small improvements to the signal. In previous static measurements using wire electrodes in a flat-cell [5] a period of time was needed for $MV^{.+}$ to accumulate before it could be detected. Accumulation is not possible in a flow-cell, at a certain time the concentration gradient of $MV^{.+}$ along the channel will reach steady-state. The decay of the $MV^{.+}$ is not visible in the CV in Figure 2 because of the experimental timescale of such experiments. Chronoamperometry at more negative potentials (-1.1 V vs the Pt pseudo-reference), did not give an EPR signal in *in-situ*, nor blue colouration in *ex-situ* measurements. This is consistent with the CV of MV where at a second reduction wave $MV^{.+}$ undergoes a second electron transfer to give neutral and diamagnetic MV^0 [7]. During CVs of 50-100 mV/s with a flowing solution 0.00083 ml/s to 0.00417 ml/s, colouration at the first reduction wave, followed by discolouration at the second reduction wave confirms the two-step reduction

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process. This precise control over the potential highlights the stability of the pseudo-reference potential arising from our channel flow-cell design. Furthermore, the EPR spectra in Figure 3 B and C clearly show that our design is suitable for the electrochemical generation and detection of radicals.

Redox couples of BQ in both water and ACN show the same peak shape indicating that the solvent does not cause this shape change compared to bulk experiments. The redox couple of MV does not show any distortions due to the dimensions or the electrode configuration of the cell. This may be due to the positive charges of the MV species which allows migration or better kinetics of the reaction.

<Figure 3>

Figure 3: (A) CV of 5 mM BQ in acetonitrile with 0.1 M TBAP with a flow speed of 0.00333 mls^{-1} and 50 mV/s and of 5 mM methyl viologen in H_2O + 0.2 M Na_2SO_4 with a flow speed of 0.00167 ml/s and 100 mV/s. (B) EPR spectrum of electroreduction of the benzoquinone solution at -0.5 V and flow speed of 0.00167 ml/s at 0.15 mW microwave power and 9.763 GHz microwave frequency. (C) EPR spectrum of electroreduction of the methyl viologen at -0.8 V and flow speed of 0.00667 ml/s at 1.00 mW microwave power and 9.746 GHz microwave frequency.

Conclusions

In this work we designed a new modular electrochemical EPR flow cell featuring (i) the use of POM as a material suitable for the setups combining electrochemistry and EPR (ii) an increased modularity and surface reproducibility in order to have rapid change of electrode material, (iii) an enhanced potential control by reducing electrode distances and optimizing the position of the pseudo-reference electrode, and (iv) a well-defined hydrodynamic flow pattern by the chosen dimensions of the channel. The flow cell was validated in both aqueous and organic media using example reactions which are common for these kind of set-ups. With this work, we have created an experimental platform that is imperative for a successful implementation and design of new electrocatalysts. In future work, this set-up will be used to investigate other reactions and electrocatalysts in combination with microscopic techniques for better catalyst screening.

Acknowledgements

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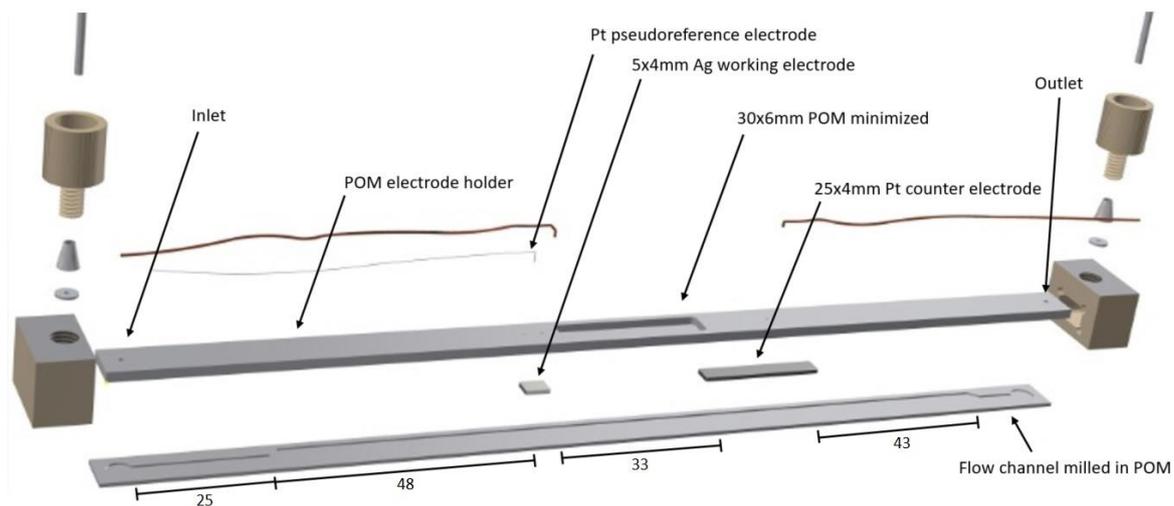
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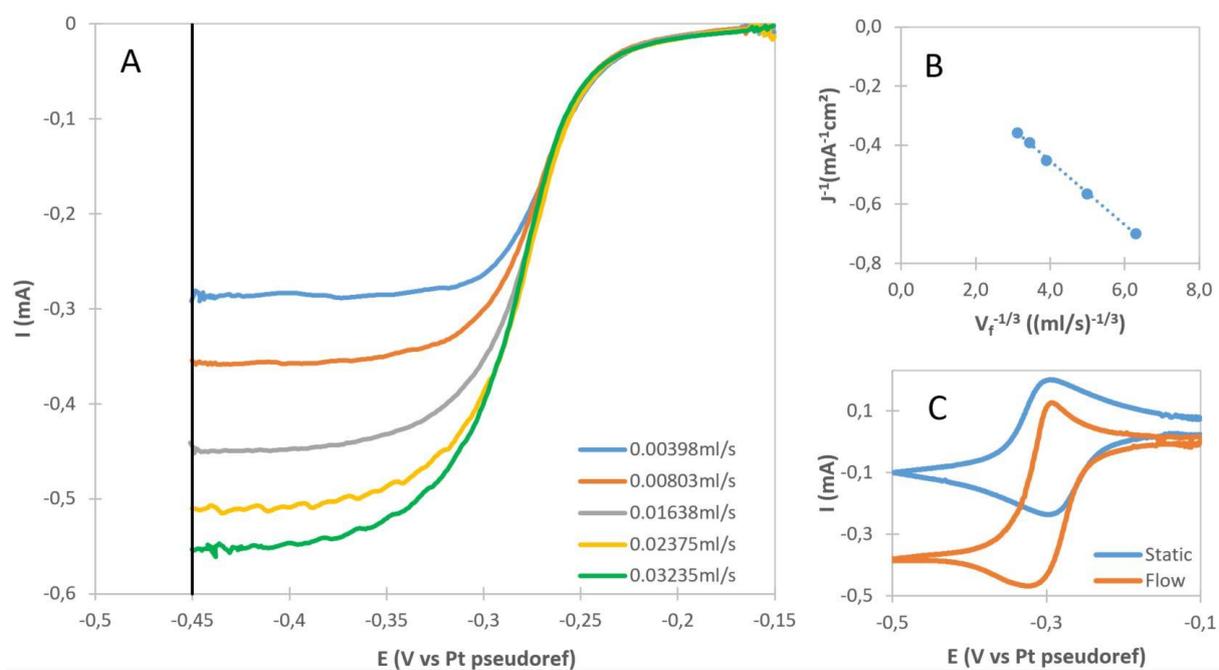

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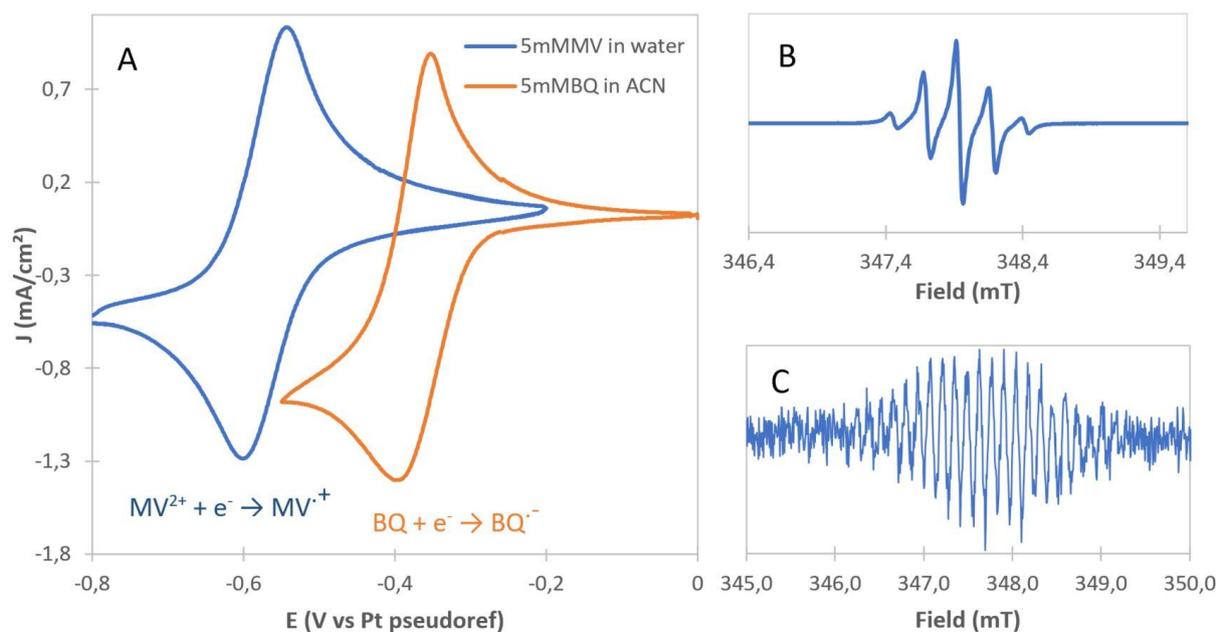
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