Rates of mass transfer to patch electrodes in disturbed flows using oxygen reduction under limiting current conditions

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A B S T R A C T

The cases of a sudden pipe expansion and a sudden pipe contraction are simulated within a flow loop-based test section designed to approximate disturbed conduit flow. Mass transfer rates to patch electrodes at selected positions within the test section have been measured using a limiting current methodology applied to oxygen reduction at copper in 3.5% wt./vol. NaCl. Using both large-scale polarisation linear sweep voltammetry and a potential step current transient technique with hydrodynamic steps, absolute and relative rates of oxygen mass transfer have been examined as a function of Reynolds number and location within the test section. The highest rates of oxygen transfer were observed both within the high velocity area of the test section and close to known regions of flow disturbance. Under the flow conditions used, patch electrode mass transfer relates to wall shear stress, which allowed areas of high mean and high fluctuating wall shear stress to be identified.

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1. Introduction

The determination of mass transfer controlled reaction rates at solid interfaces has consequence in chemical engineering for predictions relating to materials performance [1–3], metal finishing [4,5] and general heat and mass transfer [6–9]. Of particular interest to this current work is the practical simulation of flow-influenced corrosion processes in disturbed pipe flow. A flow loop-based electrochemical cell (test section) has been specifically designed to simulate disturbed flows immediately downstream of a sudden pipe expansion and a pipe contraction [10–12]. Fig. 1 describes a cross sectional view through the apparatus. The flow loop test section assembly used in here contains the eight electrodes as indicated in the figure. Many of these electrodes could experience distinct conditions of fluid flow during the experimental period, which may, in turn, affect localized rates of mass transfer.

In terms of mass transfer, the electrochemical reduction of oxygen in dilute chloride media, such as aqueous sodium chloride (NaCl), is well understood for standard conditions [13]. This reaction has previously been adapted to examine mass transfer controlled electrochemical processes in undisturbed flows using electrodes produced from copper [14,15] and copper alloys [16,17]. Furthermore, for patch electrodes of sufficiently small dimension in the flow direction, where the mass transfer layer lies within a viscous wall layer with a linear velocity profile, mass transfer is proportional to (wall shear stress)$^{1/3}$ [18]. Consequently,

mean and fluctuating wall shear stress can be obtained from instantaneous rates of mass transfer, thus providing data for estimation of mechanical forces on surface films as a function of flow conditions.

Under limiting current conditions the reduction of oxygen proceeds *via* a four electron exchange [13]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

from which a mean surface averaged value of the mass transfer coefficient (k_m), which is a rate constant for mass transfer for oxygen, can be determined with the application of the limiting current method [19,20]. Values of k_m measured for each electrode can then be used to determine the Sherwood number (Sh):

$$Sh = \frac{k_m \ell}{D}. \tag{2}$$

where D is the temperature dependent diffusion coefficient of the electro-active species and ℓ is the critical dimension of the flow geometry.

Thus, although a requirement of corrosion testing may demand a change in an ambient condition, such as temperature, the cathodic behaviour of the oxygen electrode can be fully characterised using a steady turbulent flow regime prior to analyses of disturbed turbulent flows. Applicable electrode geometries include fully developed pipe flow [19] or the rotating cylinder electrode (RCE) [21], the latter of which was used in this investigation to determine the diffusion coefficient for oxygen at 35 ± 2 °C.

The primary aim of this work is an empirical quantification of the relative rates of surface averaged mass transfer and fluctuating
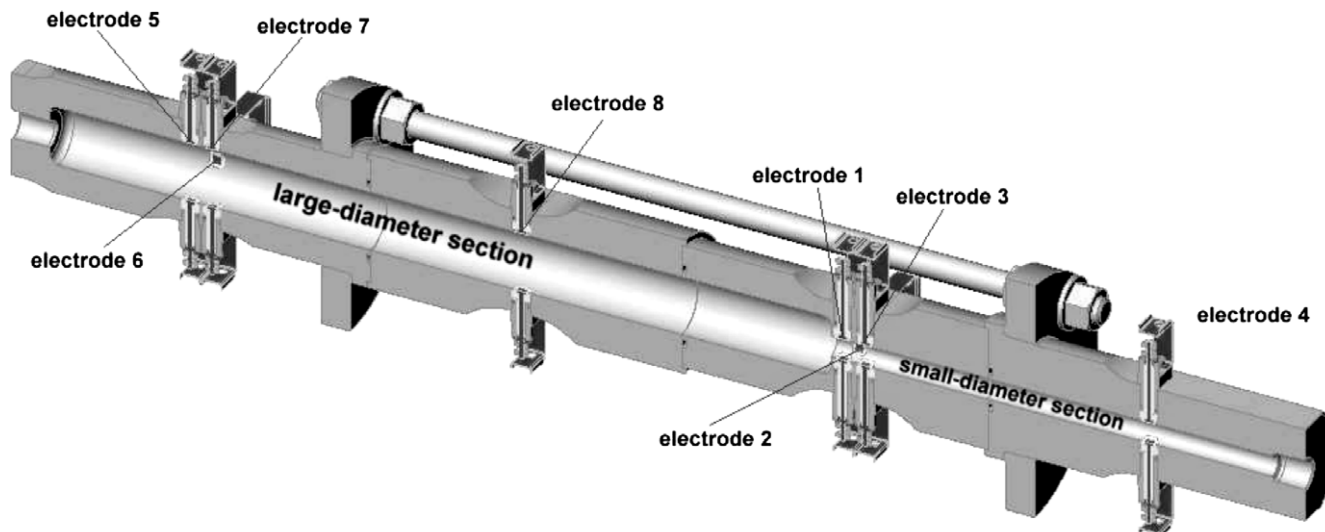
Fig. 1. Sketch of test section showing the positions of each of the eight patch working electrodes. The material of construction of the body of the test section was nickel 200.

wall shear stress to the patch electrodes at a non-standard temperature. The results of the analyses are to be incorporated into further examinations of erosion–corrosion within full-scale geometries relating, for example, to pipe transfer and heat exchanger apparatus.

2. Experimental procedure

2.1. Electrolyte

Analytical grade NaCl was used to produce an aqueous 3.5% wt./vol. (0.60 mol dm^{-3}) solution. All experiments were performed at an electrolyte temperature of 35 °C (308.15 K). A kinematic viscosity (ν) value of 0.00751 cm^2 s^{-1} at 35 °C was taken from a literature source [22]. At this temperature, a Rank Brothers Ltd. Digital Model 10 Controller was used to determine the concentration of dissolved oxygen in the bulk of the solution as 6.9 ppm (2.3×10^{-4} mol dm^{-3}).

2.2. Test section and flow loop apparatus

Both the flow loop (Fig. 2) and the associated experimental test section (Fig. 1) used in this work were designed and constructed at The University of Queensland, Australia for testing of aggressive neutral and caustic electrolytes. The majority of the apparatus was constructed from nickel 200 (UNS N02200). The loop component materials, loop manufacture and construction of the auxiliary systems have been fully described elsewhere [10–12]. As indicated in Fig. 2, the apparatus consisted of a main test loop (12.7 mm nominal diameter nickel tube) with a by-pass line. Major components of the loop included the in-house designed experimental test section, Foxboro model IMT25-A flow meter and Pressure Products Industries high-pressure nickel 200 lined turbine pump and autoclave.

The test section was designed to enable the entering fluid to experience a sudden pipe expansion into a relatively large diameter (d) section (diameter expansion from 13.7 to 38.1 mm). The overall length of the large-diameter section was 500 mm. Beyond this length, a sudden pipe contraction, resembling a pipe entry, returns the geometry back to d = 13.7 mm. The fluid then continues along the remaining 300 mm of the small-diameter section until it exits the test section. A reference electrode port communicated indirectly to the centre of the test section at 90° via a nickel 200 cooling jacket and AISI 316 (UNS S31600) stainless steel tubing
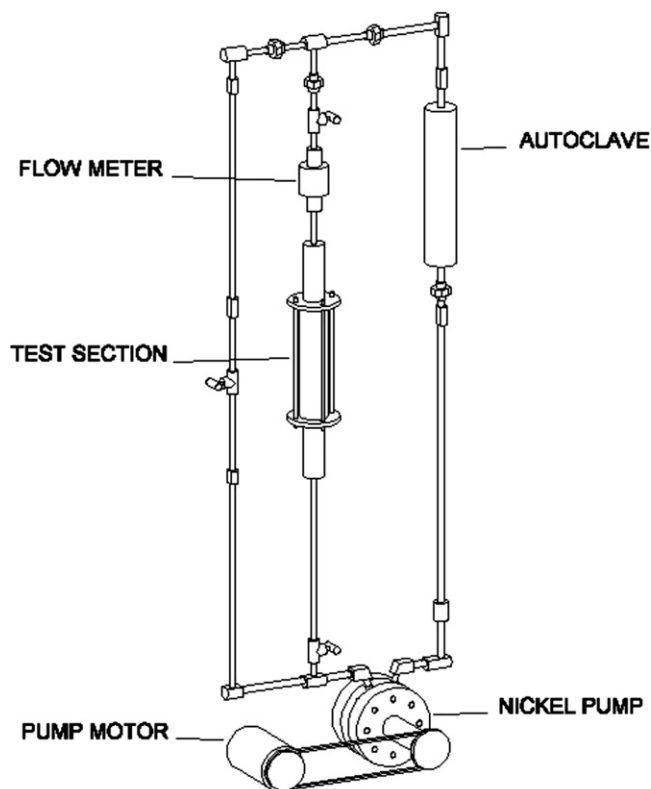

Fig. 2. Pictorial view of the nickel 200 flow loop (overall height ≅ 3 m).

(d = 6.35 mm). The reference electrode was a Hamilton Mecoref 238950 saturated silver/silver chloride (SSC$_{[sat.]}$) electrode. For the testing described in this work, a large surface area of nickel 200 was used as the counter electrode material. Oxidation of this electrode to give soluble nickel-based species was assumed to occur in the chloride-based solution. However, the resulting contamination had an insignificant influence over the limiting current response due to the low concentrations of contamination at the low values of applied current densities and the large volume of test solution (~2 dm^3). The electrolyte was also replaced between each measurement.