JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 481–488

Dynamic analysis of charge transport in fluidized bed electrodes: Impedance techniques for electroactive beds

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Received 12 March 1993; revised 25 October 1993

Impedance techniques are used to investigate the average dynamic behaviour of a fluidized bed of gold-coated beads in potassium ferri-ferrocyanide/NaOH solution. A transmission line is used as a model. The main features of the fluidized bed are correctly interpreted, especially the capacitive high frequency impedance related to the intermittent contacts between the particles. The use of a non-uniform transmission line is attempted in order to study the influence of a distance dependent charge transfer mechanism in the bulk of the fluidized bed.

1. Introduction

In a previous paper [1], it was shown that the average dynamic behaviour of a fluidized electroinactive bed can be described from the impedance measured between the current feeder and the reference electrode located above the bed. A description of charge transport in fluidized bed electrodes based on the model of Newman and Tobias [2] was proposed to explain the experimental results in terms of impedances. The main result obtained on the electroinactive system investigated (gold/NaOH interface) is the evidence for a capacitive/resistive contact impedance between the particles which leads to an extra parasitic overvoltage.

In this paper the previous model is applied to an electroactive bed where a redox reaction occurs between the gold-coated beads and the electrolyte.

2. Experimental results

The experimental arrangement of the fluidized bed is the same as in the previous paper [1]. The measurement of the potentials were made by means of a composite probe. The potential of the metallic phase, ϕ_m, was determined by a gold electrode of bead form and the potential of the electrolytic phase, ϕ_s, by a saturated calomel reference electrode. The impedance measurements were carried out using a frequency response analyzer (FRA Schlumberger 1250) and the experimental arrangement depicted in Fig. 1 where the fluidized bed is polarized by a potentiostat.

Before investigating the impedances which characterize the fluidized bed, preliminary studies involving current/voltage curves and potential distribution inside the fluidized bed were performed with 1 M NaOH electrolyte containing 0.015 M of potassium ferrocyanide and 0.001 M of potassium ferricyanide. The fluidized bed behaviour was tested in various regimes with the electrolysis current limited either by reaction kinetics or by mass transport of the electroactive species.

2.1. *Current voltage curves*

Figure 2 shows steady-state current/voltage curves, I/V (where $V = \phi_s(x) - \phi_m(0)$ with $x = 18\,\text{mm}$) obtained potentiostatically for various values of the electrolyte velocity, with the composite probe located 2 mm above the bed. When the bed was completely fluidized ($u \geqslant 1\,\text{cm}\,\text{s}^{-1}$) its height was about 16 mm. Therefore the local potential values corresponding to the current/voltage curve of Fig. 2 were taken at about 18 mm from the current feeder. At high velocity ($u = 1.4\,\text{cm}\,\text{s}^{-1}$), where the bed was completely fluidized, the current showed very large fluctuations and the average current was estimated by means of an oscilloscope.

These curves show a well defined diffusion limited current in the cathodic domain as the potassium ferricyanide had a much lower concentration than the potassium ferrocyanide. The limiting current increases as the electrolyte velocity increases, especially in the fixed bed situation. However, as soon as the bed becomes fluidized ($u = 1.4\,\text{cm}\,\text{s}^{-1}$), the plateau is less well defined and the limiting current increased more slowly than expected.

When the electrolyte velocity between the particles increased, the anodic current also increased so long as the bed remained motionless. However, as soon as the fluidization threshold was exceeded, the current diminished rapidly when the particles were separated and in motion. This feature showed that

0021-891X