JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 801–809

Dynamic analysis of charge transport in fluidized bed electrodes: impedance techniques for electro-inactive beds

C. GABRIELLI, F. HUET, A. SAHAR

LP15 du CNRS, Physique des Liquides et Electrochimie, Laboratoire de l'Université Pierre et Marie Curie, Tour 22, 4 place Jussieu, 75252 Paris Cedex 05, France

G. VALENTIN

Laboratoire des Sciences du Génie Chimique, ENSIC, Nancy, France

Received 30 August 1990; accepted 9 February 1992

A model of charge transport in fluidized bed electrodes, based on the model of Newman and Tobias, is proposed. It explains the dynamic behaviour of these particulate electrodes in terms of a.c. impedance thanks to a description based on a transmission line. In the case of gold beads in 1 M NaOH solution, the impedance related to the mean contact between the particles, the interfacial impedance of the particle–solution and the solution resistivity can be obtained.

1. Introduction

In electrolysers of practical interest, the active area per unit volume of electrode is a parameter of great importance. The fluidized bed electrolyser has been proposed to optimize this parameter as described through two patents [1, 2] in 1966. To date, little commercial use of this electrolyser has been made. A few applications can be found for fuel cells, organic electrosynthesis, precious metal electrowinning from very dilute solutions, non-precious metal mining and batteries. If the working conditions of the electrolyser are not well chosen it consumes more energy than a conventional electrolysis cell. This may be due, when high current densities are used in the counter electrode chamber: (i) to a greater resistance to current flow related to the intermittent contact between the conducting particles and (ii) to concomitant potential distributions in the bulk of the fluidized bed which lead to parasitic gas evolution or incomplete use of the whole active surface. Therefore, the use of the fluidized bed electrolyser has hitherto been limited because its electrical and electrochemical behaviour are insufficiently understood [3–11].

A fluidized bed electrode consists of solid metallized or metallic particles dispersed by an upward flow of a fluid. The fluid is injected through a perforated distributor, through a calming section which imposes a uniform fluid velocity over the whole cross-section of the bed. With a sufficiently high fluid velocity the particles are suspended by the fluid and the whole bed of particles becomes mobile. A current feeder is installed in the bed; this can be positioned so that the current lines are either perpendicular or parallel to the electrolyte flow. This electrolyser has the advantages of fixed particulate (packed bed) electrodes (large specific area, better mass transport due to the forced flow of the electrolyte), but in addition the particles are mobile. Therefore, the material may be easily added to or taken from the cell and metal deposition does not necessarily cause difficulties with clogging of the electrode. This allows the total electrolysis current to be considerably increased. However, in addition to the potential distribution in the solution that characterizes all porous electrodes, the loss of equipotentiality of the conducting matrix due to the moving metallic particles penalizes this type of electrode. The potential transients due to the intermittent contacts between the particles and between the particles and the current feeder, affect the electrochemical reactions that take place on the surface of the particles and, therefore, the global performance of the electrolyser. It is not satisfactorily established yet how the current is transferred to the individual particles. For the particles to act as unipolar rather than bipolar electrodes, electrons must be transferred from one particle to another by electronic conduction, being generated or discharged by the appropriate electrode reaction at the surface of one particle only.

Many investigations [12] of the steady-state behaviour (current–voltage curves, potential distribution diagrams) have been carried out and have validated the model of porous electrodes proposed by Newman and Tobias [13]. This approach considers the fluidized bed electrode as a system of two pseudo-continuous phases characterized by different conductivities. In addition, the global behaviour of the fluidized bed electrode is assumed to be similar to that of a one dimensional reactor. All the studies show the important influence of the electronic conduction of the dis-

0021-891X/92