

Mass transfer behaviour of gas-evolving particulate-bed electrode

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Rates of mass transfer for the cathodic reduction of potassium ferricyanide at a particulate bed of graphite supported on a horizontal nickel disc were studied under H₂-evolving conditions. Variables studied were: H₂ discharge rate, particle size and bed height. The rate of mass transfer was found to increase to a maximum in the presence of the bed which was about 4.5 times compared to that of the supporting disc. The rate of mass transfer was found to increase with H₂ discharge rate, particle size and bed height. Polarization was measured for beds of different particle size and it was found that the presence of the bed increased polarization especially at relatively high current densities, the increase in polarization was independent of particle size of the bed. Comparison with an O₂-evolving particulate electrode was made and possible practical applications were pointed out.

Symbols

- K mass transfer coefficient (cm s⁻¹)
 V H₂ discharge rate (cm³ cm⁻² s⁻¹)
 I current consumed in reducing potassium ferricyanide (A)
 A supporting disc area (cm²)
 F Faradays constant (96 500 C mol⁻¹)
 C Potassium ferricyanide concentration (mol cm⁻³)
 Z number of electrons involved in the reaction

1. Introduction

Electrochemical reactors based on fluidized- and packed-bed electrodes have been arousing great interest owing to the high space-time yields resulting from their high specific area and high mass transfer coefficient. The performance characteristics of fluidized- and packed-bed electrodes have been studied by many authors using diffusion-controlled reactions with a current efficiency of 100%. In most of these studies, gas evolution was avoided. Bennion and Newman [1] have reported that gas evolution has a deleterious effect on the performance of the electrode. Goodridge and Ismail [2] tested the performance of the fluidized-bed electrode using the chlorine discharge reaction;

this reaction is a charge transfer controlled reaction and therefore does not provide information about the mass transfer characteristics of the fluidized-bed electrode when used in conducting mass transfer controlled reactions. Since many industrial electrochemical reactions take place simultaneously with oxygen or hydrogen evolution, it is worthwhile studying the effect of these gases on the performance of packed- and fluidized-bed electrodes and in particular on the rate of mass transfer at these electrodes.

In a previous study, Sedahmed and Shemilt [3] studied the mass transfer characteristics of a gas-evolving packed-bed electrode composed of an array of closely packed screens, and they found that the rate of mass transfer was increased by gas evolution according to the equation

$$\log K = a + 0.285 \log V (\text{for H}_2 \text{ or O}_2 \text{ evolution}).$$

Fouad and Sedahmed [4] studied the mass transfer characteristics of an oxygen-evolving particulate electrode composed of graphite particles supported on a flat disc feeder electrode. They found that the rate of mass transfer at the particulate oxygen-evolving beds was lower than that at the supporting disc at different oxygen discharge rates except for large particle size where the behaviour of the bed approached that of the supporting disc.

The present investigation is concerned with the study of the mass transfer characteristics of hydrogen-evolving particulate electrodes using the cathodic reduction of potassium ferricyanide. No mechanical circulation of the electrolyte through the bed was used, motion of the bed particles being induced by the evolved hydrogen bubbles.

2. Experimental technique

The cell used (Fig. 1) comprised a 1 l glass container of 12.5 cm height and 10 cm diameter, divided into two compartments by a tight PVC porous diaphragm. The inner compartment (4.7 cm diameter) formed the cathode and consisted of a bed of graphite granules supported on a nickel disc of 4.7 cm diameter. The anode consisted of a cylindrical wire gauze made of stainless steel and placed in the outer compartment. The electrical circuit consisted of a 12 V d.c. source, a rheostat and a multirange ammeter connected in series with the cell. Current was fed to the nickel disc and the bed through a nickel wire (insulated except at the contact with the bed). A voltmeter was connected in parallel with the cell to measure its potential. Before each run the cell was filled with a solution containing 0.2 M potassium ferricyanide + 0.2 M potassium ferrocyanide + 2 N sodium hydroxide. Electrolysis was carried

out above the limiting current for the cathodic reduction of potassium ferricyanide for a period which gave about a 3–5% decrease in potassium ferricyanide concentration. After each run the solution in the inner compartment was stirred well and a sample was taken for analysis of ferricyanide content using iodometry [5]. The mass transfer coefficient was calculated using the equation

$$\frac{I}{AZF} = KC$$

The current (I) consumed in reducing potassium ferricyanide was calculated using Faraday's law and the analytically-determined decrease in potassium ferricyanide concentration. The gas discharge rate was calculated by subtracting the current consumed in reducing the ferricyanide from the total current passing and then applying Faraday's law to obtain the mass of hydrogen evolved; this mass was converted into a volume using the gas law. In all cases the surface area (A) was based on the area of the supporting disc. A similar procedure was used by different workers [6–14] to determine the mass transfer coefficient and gas discharge rate in studying mass transfer at gas-evolving electrodes. Sedahmed [13] has ruled out the possibility of chemical reaction between the electrolytically evolved H_2 and potassium ferricyanide.

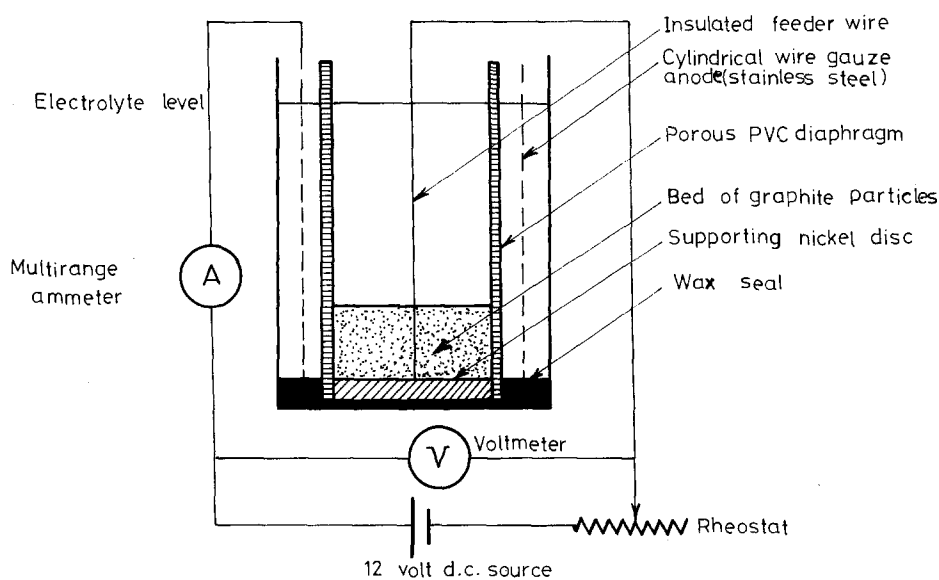


Fig. 1. Cell and electrical circuit.

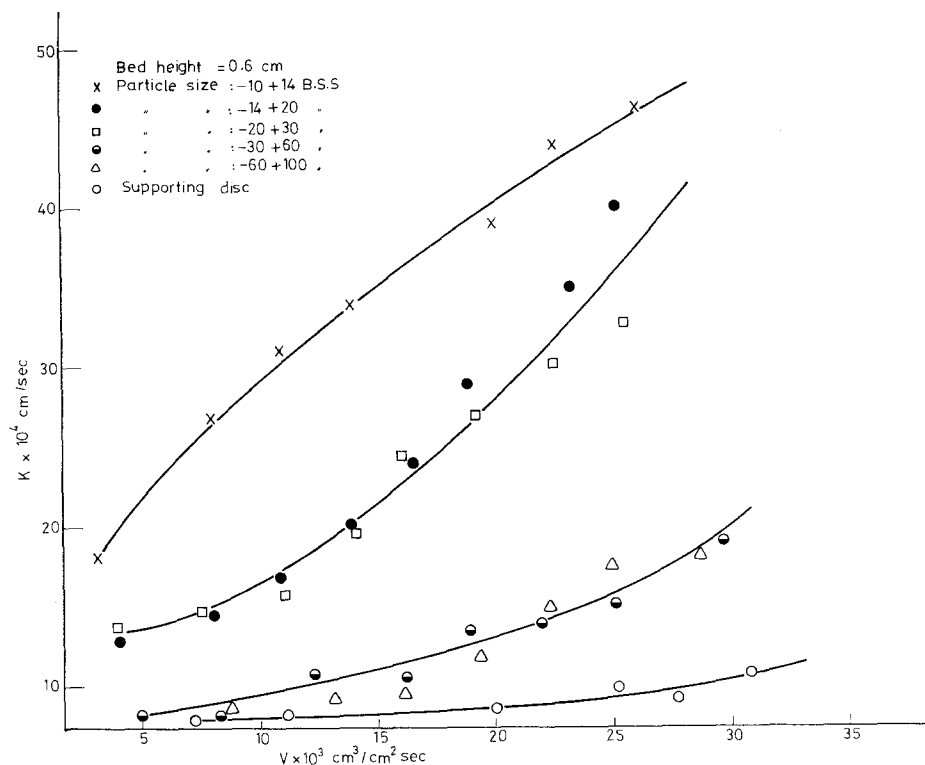


Fig. 2. Effect of H_2 discharge rate on the rate of mass transfer at beds of different particle size. (B.S.S. stands for British standard specification.)

3. Results and discussions

At relatively low H_2 discharge rates and large particle size, the electrode acts as a fixed bed. H_2 bubbles, by virtue of their small size, penetrate the bed easily through the voids, along with the displaced solution. The friction between the upward-moving gas-liquid dispersion causes the particles of the bed to vibrate in their positions. With increasing gas discharge rate or decreasing particle size, bed fluidization begins, the degree of bed expansion is higher the higher the gas discharge rate and the lower the particle size.

Fig. 2 shows the effect of H_2 discharge rate on the mass transfer coefficient of the cathodic reduction of potassium ferricyanide at beds of different particle size. For all particle sizes, the presence of the bed leads to an increase in the mass transfer coefficient over that of the supporting disc electrode. For a given particle size, the higher the rate of H_2 discharge, the higher the rate of mass transfer.

For a given H_2 discharge rate, the larger the

particle size of the bed, the higher the mass transfer coefficient. The observed increase in the mass transfer coefficient due to the presence of the bed ranges from 1.5–4.5 times depending on the gas discharge rate and particle size. This increase in the mass transfer coefficient compares favourably with the value observed in the case of non-conducting fluidized beds used to enhance mass transfer at a conducting electrode surface [15–18]. This similarity suggests that the bed in the present work is mainly acting as a non-conducting bed, probably because the evolved H_2 bubbles hinder the electrical contact between the graphite particles and the supporting disc. The mass transfer enhancement caused by the presence of graphite particles can be attributed to the continual penetration and disruption by these particles of the diffusion layer at the supporting disc. The increase in the mass transfer coefficient with H_2 discharge rate and particle size is explained by the increase in the momentum of the particles with a consequent increase in their ability to promote turbulence when they strike the diffusion layer at the

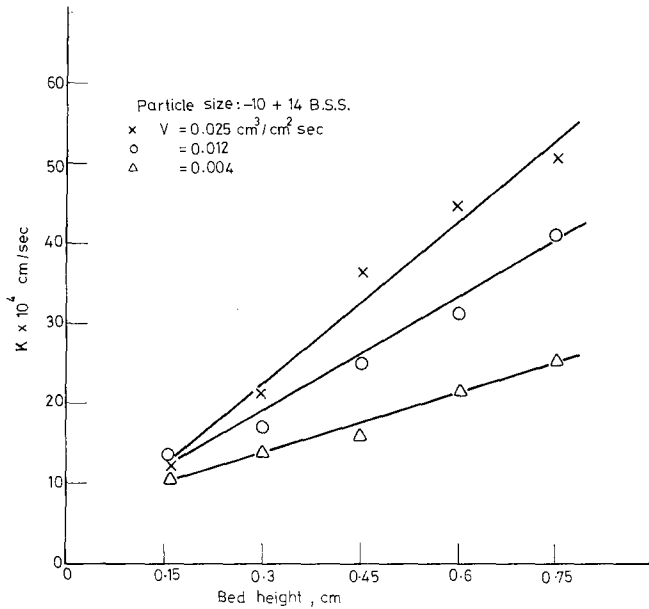


Fig. 3. Effect of static bed height on the mass transfer coefficient.

disc electrode. Similar findings have been reported in the case of heat and mass transfer in two-phase fluidized beds [15-19].

Fig. 3 shows the effect of bed height on the mass transfer coefficient for different H_2 discharge

rates; the mass transfer coefficient increases with bed height at different H_2 discharge rates.

It would be of interest to compare the behaviour of an O_2 -evolving particulate electrode [4] with that of a H_2 -evolving electrode. As mentioned

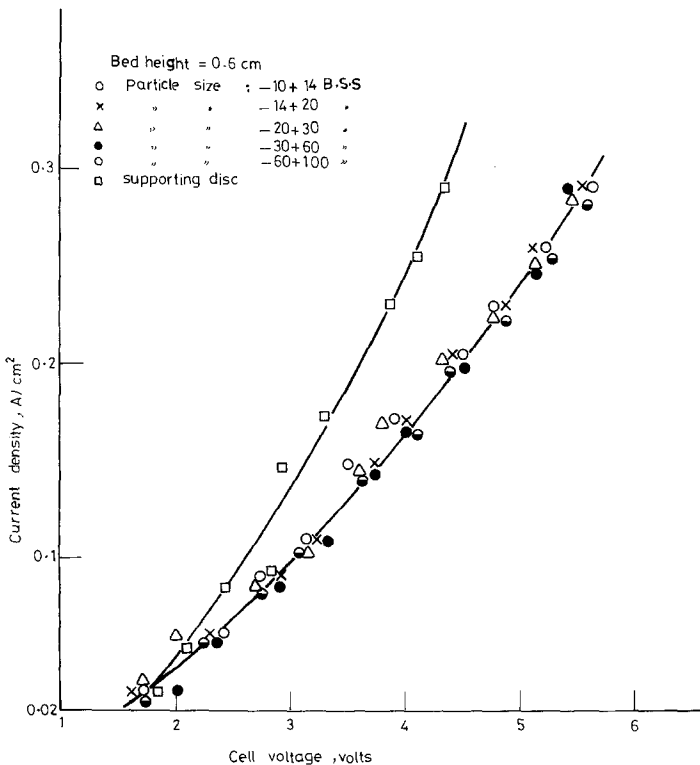


Fig. 4. Polarization at beds of different particle size.

before, Fouad and Sedahmed found that mass transfer rates at an O₂-evolving particulate electrode were less than those of the supporting disc electrode except at relatively large particle size where the rate of mass transfer approached that of the supporting disc electrode. The difference in behaviour between an O₂-evolving particulate electrode and a H₂-evolving particulate electrode may be attributed to the difference in the bubble size. Janssen and Hoogland [14] found that O₂ bubbles evolved from alkaline solutions are much larger than H₂ bubbles, and that O₂ bubbles tend to coalesce in alkaline solutions while H₂ bubbles have no such tendency. Small H₂ bubbles can find their way easily through the voids of the bed while large O₂ bubbles find it difficult to pass through the voids of the bed and reside at the supporting disc until a sufficient pressure is developed to create channels in the bed through which bubbles can escape. The large residence time of O₂ bubbles at the disc electrode leads to a blanketing of part of its surface with a consequent reduction in its area and a corresponding reduction in the apparent mass transfer coefficient.

Fig. 4 represents current–potential relationships at the supporting disc electrode and at beds of different particle size. Polarization at particulate beds is higher than that at the supporting disc. The difference in polarization between the bed and supporting disc is independent of particle size but increases with current density. The increase in cell polarization in the presence of the bed may be attributed to the increased resistance of the cell caused by the presence of the particles and the delay in H₂ bubble escape from the solution.

In view of the substantial increase in the rate of

mass transfer at H₂-evolving particulate electrodes, the electrode can form the basis of an industrial electrochemical reactor used to conduct diffusion-controlled reactions taking place with a current efficiency less than 100%.

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