

# MECHANISM OF CHARGE TRANSFER IN THE DISCONTINUOUS METAL PHASE OF A FLUIDIZED BED ELECTRODE

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**Abstract**—From measurements of double layer capacity, collision frequency and contact time during collision, it is concluded that models for charge transfer in the discontinuous phase of a fluidized bed electrode that are based on ideal particulate fluidization cannot explain metal phase resistivities, experimentally observed.

Based on a literature survey it is shown that not only gas–solid but also liquid–solid fluidization is at least partially aggregative.

A preliminary model for charge transfer in the discontinuous phase, based on aggregative fluidization, is derived.

### NOMENCLATURE

$a$	ribbon of cubic cluster	(m)	$\Delta V_b \Delta V_u$	change in potential of double layer and known capacity respectively, after closing $S$ (Fig. 4)	
$\bar{c}$	bulk concentration of electrolyte	(kmol/m <sup>3</sup> )	$V_a - V_s$	cell potential	(V)
$C_d$	double layer capacity per m <sup>2</sup> particle surface	(F/m <sup>2</sup> )	$\epsilon$	bed height/static bed height	(V)
$C_d^0$	double layer capacity per particle	(F)	$\epsilon_0$	porosity of static bed	
$C_{da}^0$	double layer capacity of aggregate	(F)	$\nu$	number of collisions per particle per second	(s <sup>-1</sup> )
$C_u$	known capacity	(F)	$\nu_a$	number of contact bridges per aggregate per second	(s <sup>-1</sup> )
$Fr$	Froude number, defined by (10)	(F)	$\nu'_a$	<i>idem</i> , per aggregate surface particle	(s <sup>-1</sup> )
$g$	gravity constant	(m/s <sup>2</sup> )	$\rho_m$	effective specific resistivity of the discontinuous phase	(Ωm)
$i$	current density in discontinuous phase per unit cross sectional area	(A/m <sup>2</sup> )	$\rho_s$	effective specific resistivity of the solution phase	(Ωm)
$I_p$	net charge transfer per second per particle	(A)	$\tau$	time constant for charge sharing during a particle collision	(s)
$l(l_a)$	effective distance between two particle (aggregate) centres in $x$ -direction	(m)	$\tau_a$	time constant for charge sharing of two aggregates during a particle bridge	(s)
$\Delta l$	effective interparticle surface distance in $x$ -direction	(m)	$\phi_m$	potential of discontinuous phase	(V)
$\Delta l_a$	distance between adjacent aggregate surfaces	(m)	$\phi_s$	solution potential	(V)
$n$	number of particles per m <sup>3</sup>	(m <sup>-3</sup> )			
$n''$	number of particles per m <sup>2</sup> cross section	(m <sup>-2</sup> )			
$n_a$	number of particles per aggregate	(m <sup>-3</sup> )			
$N_a$	number of aggregates per m <sup>3</sup>	(m <sup>-3</sup> )			
$r$	radius of particles	(m)			
$R$	resistance of double layer	(Ω)			
$R_u$	known resistance	(Ω)			
$t_c$	contact time of a two-particle collision	(s)			
$t_{ca}$	life time of one particle-bridge between two aggregates	(s)			
$U_{mf}$	minimum fluidisation velocity	(m/s)			
$x$	direction of maximum potential gradient	(m)			

### INTRODUCTION

In designing a fluidized bed electrode (*fbe*), the effective *dc* specific resistivity of the discontinuous phase ( $\rho_m$ ), plays a major role. Both theoretical and experimental knowledge of this parameter, however, are relatively poor. Experimental data for copper coated glass spheres of about 500 μm are given in Fig. 1.

In fact, the picture is more complicated because of local bed disturbances near the distributor, resulting in a substantially lower resistivity close to the grid[2].

In a pioneering article, Fleischmann and Oldfield[3] derived an expression based on a model of ideal particulate fluidization in which complete or partial charge sharing occurs during elastic collisions of single particles. After substitution of estimated

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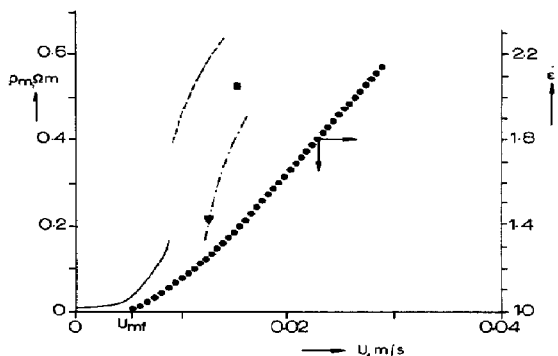


Fig. 1. Metal resistivity and bed expansion as a function of superficial liquid velocity for copper-coated glass spheres of about 500 μm dia. ---: [1], 1M H<sub>2</sub>SO<sub>4</sub>; ---: [2], 1M H<sub>2</sub>SO<sub>4</sub>; —: our experiments, 1M KCl; ■, ▼: our experiments, 1M H<sub>2</sub>SO<sub>4</sub>.

Current density  $i$  follows from:

$$i = I_p n l \tag{5}$$

where  $n$  is the number of particles per m<sup>3</sup>:

$$n = 3(1 - \epsilon_0)/(4 \pi r^3 \epsilon) \tag{6}$$

and  $l$  can also be considered as the volume per unit area normal to the  $x$  direction that contains the particles which take care of charge transport through that unit area.

Combination of (2), (4) and (5) results in:

$$\rho_m^{-1} = 1.5(1 - \epsilon_0) C_d v r \epsilon^{-1/3} (1 - e^{-t_c/\tau}) \tag{7}$$

For  $\epsilon_0 = 0.4$ , (7) predicts a conductivity  $\rho_m^{-1}$  which is nearly a factor of four lower than obtained with Fleischmann's (3).

The difference is mainly caused by: (1) a factor of two in the assumption of effective  $l$  (Equation 4), and (2) a factor of two in (2), due to our assumption that a particle must collide twice to transport one batch of charge over distance  $l$ .

values for collision frequency  $\nu$ , double layer capacity  $C_d$ , contact time during collision  $t_c$ , and RC-time of a particle  $\tau$ , in their theoretical equation for the specific resistivity of the metal phase, they found a predicted value for  $\rho_m$  which was higher than experimental findings[1]. For this reason we measured  $\nu$ ,  $C_d$ ,  $t_c$  and  $\tau$ . The result was an even greater discrepancy between theory and experiment. Thus we concluded that a model based on ideal particulate fluidization is not realistic, at least not for practically important bed expansions below 30%.

Based on recent experimental evidence for the existence of aggregative fluidization, not only in gas-solid but also in liquid-solid fluid beds, we suggest a model for charge transfer based on the occurrence in the bed of particle aggregates in which the potential is uniform. The relation between the aggregate diameter and  $\rho_m$  can be understood qualitatively.

THE SINGLE PARTICLE COLLISION MODEL, BASED ON IDEAL PARTICULATE FLUIDIZATION

For the case of

$$(\Delta l) d\phi_m/dx \ll l d\phi_m/dx \tag{1}$$

particle potential change between two collisions may be neglected. In aqueous solutions and relatively low bed expansions, condition (1) is mostly fulfilled.

In this case, one particle transfers per second:

$$I_p = \frac{1}{2} \nu l C_d^0 (1 - e^{-t_c/\tau}) d\phi_m/dx \tag{2}$$

By substituting for  $l$ , the average particle distance, as given by:  $2\epsilon^{1/3} r$  and multiplying  $I_p$  by the number of particles per m<sup>2</sup>:

$$n'' = 1/(2\epsilon^{1/3} r)^2,$$

Fleischmann *et al*[3] derived:

$$\rho_m^{-1} = \pi C_d v r \epsilon^{-1/3} (1 - e^{-t_c/\tau}) \tag{3}$$

But due to the 3-dimensional character of particle movement the effective free length in  $x$ -direction is only half the average particle distance:

$$l \approx \epsilon^{1/3} r \tag{4}$$

Parameter values

Oscilloscopic measurements of  $\nu$  and  $t_c$  were obtained using an immobile copper particle ( $r = 2.5 \cdot 10^{-4}$  m) connected to an isolated wire in a *fbf* of copper coated glass spheres of same radius. The time interval between two collisions was highly irregular with collisions often occurring in groups. This behaviour suggested 'chain collisions'.

Figure 2 gives time averaged values of the collision frequency as a function of the bed expansion. Because the test particle is not mobile, it may disturb local bed behaviour. Therefore values for collision frequency obtained in this way can only give a rough indication of the real values for completely mobile particles.

If random particle movement on a microscale is assumed, then the measured values are a factor of two too low; but if there is a correlation between the velocities of neighbouring particles the measured values are too high. Nevertheless, it can be concluded from Fig. 2 that for bed expansions up to  $\epsilon = 1.75$ , the collision frequency is in the order of  $100 \text{ s}^{-1}$ . This value is an order of magnitude lower than the one estimated by Fleischmann *et al*[3], but is roughly in agreement with measurements of Kreysa[4].

We also measured the collision time,  $t_c$ , with the same system for  $1.2 < \epsilon < 1.5$ . In this range of bed expansion glass particles with radius of  $2.5 \cdot 10^{-4}$  m

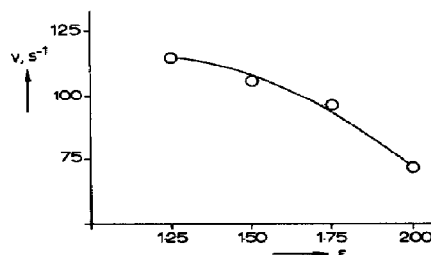


Fig. 2. Collision frequency as a function of bed expansion for copper-coated glass spheres of about 500 μm dia.

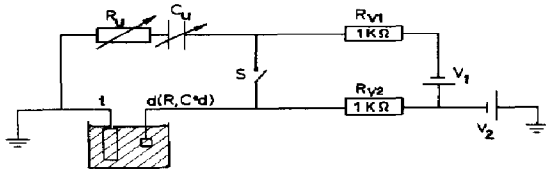


Fig. 3. Experimental set-up for measuring the double layer capacity;  $d$  = measuring electrode.

proved to have average contact times which were nearly independent of  $\epsilon$  and which were given by:

$$t_c = 2.5 \cdot 10^{-5} \text{ s}^{-1}$$

Concerning the RC-time constant,  $\tau$ , the relation used by Fleischmann[3] ( $\tau = 2r\rho_s C_d$ ) predicts an upper value based on the resistance between two particles at infinite distance[5]; but the real value will be lower. From typical values of  $r$  ( $2.5 \times 10^{-4}$  m),  $\rho_s$  ( $5 \times 10^{-2} \Omega\text{m}$ [1]) and  $C_d$  ( $0.2 \text{ F/m}^2$  (our experiments)) it follows that:

$$t_c/\tau > 4 \tag{8}$$

Thus (8) indicates complete charge sharing during collision, and so (7) reduces to:

$$\rho_m^{-1} = 1.5(1 - \epsilon_0) C_d \nu r \epsilon^{-1/3} \tag{9}$$

which indicates a linear relationship between metal phase conductivity and double layer capacity.

We have developed a relatively simple method for measuring  $C_d$  of a metal surface in electrolyte solution (Fig. 3).

After closing switch  $S$ , a charge pulse from a variable, known capacity ( $C_u$ ) flows via a variable, known resistance ( $R_u$ ) to the unknown double layer capacity  $d$  which acts as a capacity resistance element with a typical RC-time of the order of  $10 \mu\text{s}$ . Figure 4 shows the simplified electrical analogue and typical potential-time curves after closing switch  $S$ .

For the case that  $R_u C_u = R C_d$ ,  $C_d^0$  follows from:

$$C_d^0 = C_u \Delta V_u / \Delta V_d$$

Although complications may occur in practice, it has

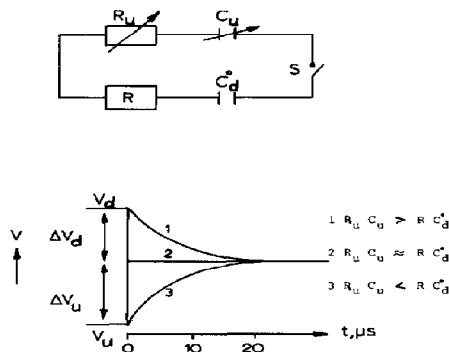


Fig. 4. Simplified electrical analogue of experimental set-up with theoretical change in potential as a function of time of known ( $\Delta V_u$ ) and unknown capacity ( $\Delta V_d$ ) after closing switch  $S$ . Different curves represent different values of the ratio  $R_u C_u / R C_d$ .

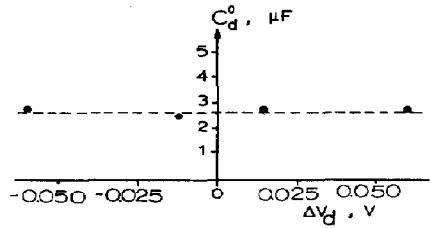


Fig. 5. Double layer capacity as a function of potential change of double layer after closing switch  $S$  ( $\Delta V_d$ ).

been shown that reliable results can be obtained[6]. For copper electrodes in  $1\text{M H}_2\text{SO}_4$ ,  $C_d^0$  proved to be independent of the applied  $\Delta V_d$  (Fig. 5) and of the measuring cell potential  $V_d - V_i$  (Fig. 6). Figure 7 shows results for copper electrodes as a function of concentration in both  $\text{KCl}$  and  $\text{H}_2\text{SO}_4$  solutions.

Predicting  $\rho_m$  from (9) with typical experimental values of  $C_d$  ( $0.2 \text{ F/m}^2$ ),  $\nu$  ( $100 \text{ s}^{-1}$ ) and  $r$  ( $2.5 \times 10^{-4}$  m) gives  $\rho_m \approx 200 \epsilon^{1/3} \Omega\text{m}$ , which is roughly a factor 1000 too high compared to the experimental values (Fig. 1). This discrepancy is too high to be explained by a possibly higher  $C_d$  (which is strongly surface dependent) or by an inaccuracy in measuring  $\nu$  because of the immobile character of the test particle.

So we conclude that a charge transfer model based on ideal particulate fluidization with single particle collisions cannot explain the metal phase conductivity observed experimentally.

#### CHARGE TRANSFER BASED ON A MODEL OF AGGREGATIVE FLUIDIZATION

In 1948 Wilhelm *et al*[7] concluded that liquid-solid fluidization is essentially particulate for systems in which

$$Fr = U_{mj}^2 / 2rg < 0.2 \tag{10}$$

With the exception of systems with heavy and large particles, all liquid-solid systems satisfy this criterion (10).

Contrary to the above, higher Froude numbers are obtained in gas-solid fluidization. In these systems

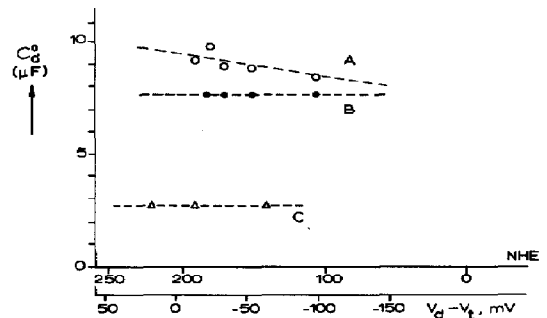


Fig. 6. Double layer capacity ( $C_d^0$ ) as a function of cell potential ( $V_d - V_i$ ) for three different copper electrodes (A, B, C).

parvoids (gas bubbles) are observed, while the particles keep in electrical contact with each other[7-10]. This type of fluidization is called aggregative. Recently, however, experimental evidence suggests that not only gas-solid, but also liquid-solid fluidization has an aggregative character[11-17]. Possibly, ideal particulate fluidization does not exist[11, 13]; instead most liquid fluidized beds fall along the transition from the ideal particulate state to fully aggregative fluidization. Apparently, the magnitude of the density difference is the main parameter determining the position along the transition[13]. Even a small density difference of only 290 kg/m<sup>3</sup>, however, is sufficient to provide a substantial tendency towards aggregative fluidization, as evidenced by the observation of large parvoids and slugs[14]. Therefore we suggested particle aggregates to play a role in the mechanism of charge transfer in the metal phase of a fluidized bed electrode[18]. Additional experimental evidence for this role has recently been reported[19, 20].

Within an aggregate, potential is considered to be uniform. Charge transfer between aggregates is possible by several mechanisms. For an average distance between two adjacent aggregate surfaces ( $\Delta l_a$ ) smaller than the particle distance, a mechanism of temporary contact bridges appears to be most likely.

Assuming cubic clusters of internal porosity  $\epsilon_0$ , each containing  $n_a$  particles, the ribbon of a cluster follows from:

$$a = \left\{ n_a \frac{4}{3} \pi r^3 / (1 - \epsilon_0) \right\}^{1/3} \quad (11)$$

while the distance between two neighbouring aggregate surfaces is given by:

$$\Delta l_a = a(\epsilon^{1/3} - 1) \quad (12)$$

For  $\epsilon_0 = 0.4$ , it follows from (12) that  $\Delta l_a$  is smaller than  $2r$  for  $\epsilon < 1.4$  and  $n_a < 500$ .

In practice the internal porosity of the aggregates will be higher than  $\epsilon_0$ . Equation (12) therefore predicts an upper value for  $\Delta l_a$ .

Analogous to the development of (3), an expression for  $\rho_m$  can be derived in terms of aggregate parameters:

$$\rho_m^{-1} = \frac{1}{2} v_a l_a^2 C_{da}^0 N_a (1 - e^{-t_{ad}/\tau_a}) \quad (13)$$

Because of the mobility of the outer particles, the number of temporary contact bridges between adjacent aggregates per unit time is most likely proportional to the number of particles at the aggregate surface:

$$v_a = b(1 - \epsilon_0)^{1/3} n_a^{2/3} v'_a \quad (\text{for } n_a > 100) \quad (14)$$

with  $v'_a$  the bridge formation frequency of a surface particle. The constant  $b$  depends on the aggregate form. For spheric and cubic aggregates  $b = 6$  and 7.5, respectively.

After substitution of:

$$N_a = (a + \Delta l_a)^{-3}$$

$$C_{da}^0 = n_a 4 \pi r^2 C_d$$

$$l_a = (a + \Delta l_a)/2$$

and of (14) into (13), the result will be:

$$\rho_m^{-1} \approx 6 n_a^{4/3} v'_a C_d a \epsilon^{-1/3} (1 - \epsilon_0)^{2/3} (1 - e^{-t_{ad}/\tau_a}) \quad (15)$$

Although  $n_a$  and  $v'_a$  are probably functions of both  $\epsilon$  and  $(\rho_m - \rho_s)$ , the relationships are unknown at present and not easy to measure. Therefore (15) does not yet give enough information for design purposes. It is clear, however, that aggregative fluidization may result in a lower metal phase resistivity, compared to particulate fluidization. For instance for  $\epsilon_0 = 0.4$ ,  $C_d = 0.2 \text{ F/m}^2$ ,  $t_{ca}/\tau_a \gg 1$  and say  $n_a = 200$  a comparative low value of  $v'_a = 10 \text{ s}^{-1}$  (see Fig. 2) is already large enough to predict from (15) the experimentally measured value for  $\rho_m$  of  $0.4 \Omega\text{m}$  for glass spheres of  $5 \times 10^{-4} \text{ m}$  dia at 30% bed expansion (Fig. 1).

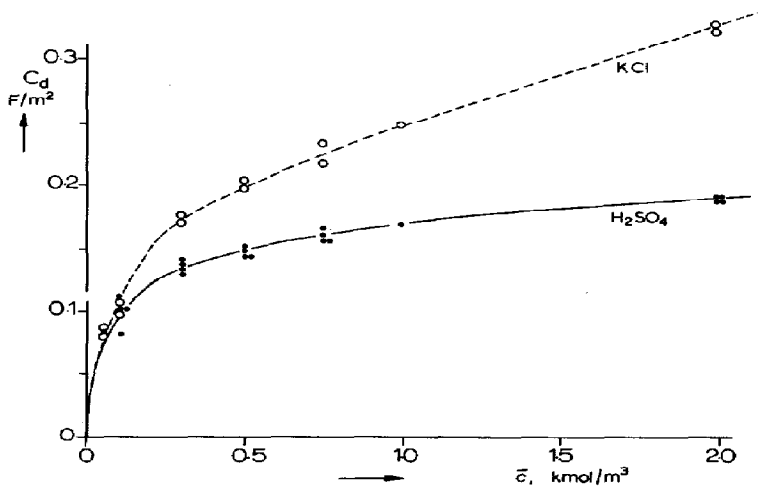


Fig. 7. Double layer capacity of copper ( $C_d$ ) as a function of electrolyte concentration;  $V_d - V_i = -20 \text{ mV}$ ,  $\Delta V_d = 30 \text{ mV}$ .

Lack of quantitative knowledge of  $n_a$  and  $v_a'$  demands that further research be conducted on microscale particle behaviour in order to provide a complete description of  $\rho_m$  from first principles.

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