

# Influence of non-conducting suspended solids onto the efficiency of electrochemical reactors using fluidized bed electrodes

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## ABSTRACT

Fluidized bed electrodes combine the advantages of a high specific electrode surface and a tolerance to reaction solutions containing suspended solids. In contrast to conventional packed-bed electrodes, which tend to get blocked when challenged with suspensions, such reaction solutions can pass freely through fluidized bed electrodes. In recent studies, we were able to show that the electric contacting between magnetic electrode particles can be improved by superposition of an external magnetic field to the fluidized bed electrode. However, these studies were conducted with plain solutions and the effect of non-conducting suspended solids on the performance of conventional and magnetically stabilized fluidized bed electrodes remained unknown. In this work, we investigate the influence of such suspension on the electrochemical conversion as well as on the conductivity of a fluidized bed electrode. Furthermore, the effect of magnetic superposition is evaluated. The results confirmed that the application of a fluidized bed electrode enabled the operation of an electrochemical model reaction process throughout the whole investigated concentration range of suspended solids (up to 40 g/L). However, the suspended solids showed a negative influence onto the electric conductivity of the fluidized bed and on the electrochemical conversions achieved. Superpositioning the fluidized bed electrode with a magnetic field of 20 mT, was able to significantly improve the electrochemical yield of the system. Therefore, magnetically influenced fluidized electrodes can be an interesting reactor type for electrobiotechnological systems combining electrochemical reactions with high densities of suspended microorganisms.

## 1. Introduction

Particle electrodes based on a high number of fine, conductive particles possess the advantage of a large specific electrode surface, a feature, which is essential for electrochemical reaction processes and high conversion yields of diluted reactants [1,2]. In the so-called fluidized bed electrode the electrode particles are fluidized by the upstream of the reactant solution, combining the advantages of a low pressure drop and a tolerance to additional solids in the feed stream [3,4]. Fluidized bed electrodes have also received considerable attention in terms of their good mass and heat transport efficiency, and the resulting even temperature distribution within the reaction system [5]. However, a major challenge in the use of fluidized bed electrodes in electrochemical processes is the controlled fluidization of the particle bed. As a result, the contacting of the individual electrode particles with each other and with the current source of the particle electrode can be a severe challenge [4,6–8]. The contacting of the individual electrode particles depends on the expansion of the particle bed, which depends, among other things,

on the flow velocity of the feed solution [6]. As a consequence, the particle contact is reduced with increasing flow velocity [6,9] and consequently the electrical resistance of the electrode bed increases [10]. This also increases the voltage drop within the electrode with increasing distance from the current source and only a small amount of the particles can participate in the electrochemical conversion [11,12].

In previous studies, it was shown that the magnetic stabilization of the fluidized bed electrode improves the contacting of the individual electrode particles within a fluidized bed electrode [10,13,14]. Here, for the first time, a magnetically stabilized fluidized bed [15–18] was combined with an electrochemical fluidized bed electrode. By placing an electric coil around the reaction system, the magnetizable electrode particles inside the reaction chamber could be influenced. During the electrochemical process, a static axisymmetric magnetic field was generated by means of a direct current within the coils. This caused the magnetic electrode particles to arrange along the magnetic field lines [18,19]. In addition, the uncontrolled movements of the electrode particles were suppressed, which improved the contact between the

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electrode particles. Using electrode particles consisting of activated carbon, carbon black and magnetite [20], it was shown that the magnetic superposition of the fluidized bed electrode with a magnetic field of 20 mT improved the effective electrode surface by a value of 400% [14]. In addition, the magnetic superposition of the fluidized bed electrode could improve the electrochemical conversion by up to 100%. Besides the magnetic influence on the electrochemical reaction process, another paper investigated the magnetic influence on the conductivity of the fluidized bed electrode [10]. By means of electrochemical impedance spectroscopy studies, it was shown that the magnetic influence near the current source of the particle electrode reduced the electrical resistance by up to 49%. On the other hand, the magnetic influence showed an even stronger effect on the apparent electrical capacitance of the electrode particles, which corresponds to the amount of particles in direct contact with each other. The magnetic influence increased the apparent capacitance by up to 400%. This value also showed good agreement with the magnetic improvement of the effective electrode surface in previous studies.

The system applying a magnetically stabilized fluidized bed electrode is a new type of electrochemical reactor, which up to now lacks a thorough investigation in terms its specific strengths and limitations. In contrast, classical fluidized bed electrodes have already been investigated for many fields and have been described in the scientific literature for a variety of applications. Examples can be found in metallurgy [2,9], energy storage and conversion [5,21,22], environmental protection [23], and water treatment [24]. Recent applications have also been described for microbial electrolysis cells [25] and also for capacitive deionization [26]. Especially with respect to the last two examples, an important point which has not yet been investigated, is the influence of non-conducting suspended solids within the reaction solution in combination with fluidized bed electrodes. Packed bed particle electrodes tend to get blocked in case of high suspended solid concentrations in the reactant solution. In contrast, fluidized bed electrodes show a high tolerance to suspended solids, as these can pass unhindered through the bed without causing a blockage. Therefore, this type of electrochemical reactor is of particular interest for electro-biotechnological systems in which redox reactions are carried out in the presence of high cell concentrations. In order to quantify and further characterize this important advantage, this work investigates the effect of model suspensions of non-conducting microparticles with varying solid content onto the efficiency of an electrochemical fluidized bed reactor. Among others, the efficiency was investigated in terms of electrochemical conversion yields and the electrical conductivity within the fluidized bed electrode. For comparison, the effect of the presence of non-conducting solids was evaluated for a conventional and a magnetically stabilized fluidized bed electrode.

## 2. Material and methods

### 2.1. Chemicals and solutions

All chemicals were analytical grade and used without further purification. Water used for all experiments was produced using a Milli-Q Ultrapure system from the company Merck Millipore (Billerica, USA). Potassium ferricyanide trihydrate, potassium ferrocyanide, potassium chloride and sodium chloride were purchased from Merck (Darmstadt, Germany). The processed resin for the 3D-printed components of the reactor device was VeroClear (mainly composed of polymethylmethacrylat (PMMA)) from the company Stratasys (Edina, USA). Amberger Kaolin was purchased from Gebrüder Dorfner GmbH & Co. Kaolin- und Kristallquarzsand-Werk KG (Hirschau, Germany).

### 2.2. Magnetic electrode particles

The magnetic electrode particles used to expand the electrode surface consisted of activated carbon, magnetite and conductive carbon black. The mean volumetric particle size distribution has been

determined to be 175  $\mu\text{m}$ . The shape of the electrode particles was largely non-spherical (see Fig. S1 A). The specific resistance of a dry, gently compressed particle bed was approximately 0.5  $\Omega\text{m}$ . A detailed description of the particles and their synthesis can be found in [10,13,14]. For further characterization the magnetization curve of the electrode particles was determined (see Fig. S1).

### 2.3. Amberger-Kaolin

The influence of non-conductive, suspended solid particles onto the electrochemical conversion as well as on the conductivity of the fluidized bed electrode was investigated using the substance Amberger-Kaolin. Kaolin is a fine, iron-free, white stone and consists mainly of kaolinite. The solid particles had a mean particle size of 8.5  $\mu\text{m}$ . The particle size distribution and an electron microscope image of Amberger-Kaolin are shown in Fig. 1.

### 2.4. Experimental determination of particle size

To determine the particle size distribution of the electrode particles as well as of the Amberger Kaolin particles an optical image analysis device (CIS 100-S, Galai, Migdal Haemek, Israel) was employed. In this instrument, the particle size is measured with the help of a rotating beam helium neon laser at 660 nm, while the laser crosses a cuvette with the particles to be analyzed. A CCD detector measures the residence time of the particles within the laser. The particle size can be calculated from the residence time and the rotation speed of the laser in the particle size range from 0.5 to 1000  $\mu\text{m}$ .

### 2.5. Magnetically stabilized fluidized bed reactor

Two different types of reactors were used to investigate the influence of suspended, non-conducting solids on the behavior of a conventional and a magnetically stabilized fluidized bed electrode. The housing of the two developed fluidized bed reactors was designed using the CAD Software Inventor 2020 (Autodesk, San Rafael, USA) and manufactured using a 3D printer (Objet Eden260VS, Stratasys, MN, USA).

To investigate the effect of the non-conducting suspended solids onto the electrochemical conversion of the fluidized bed electrode system, a fluidized bed reactor with two electrode chambers was used (see Fig. 2A). The two electrode chambers were separated from each other by means of a cation exchange membrane, so that no convective mass transfer could take place between the chambers. The inner working electrode chamber (15 mm inner diameter and 10 cm length) was designed to enlarge the working electrode by means of the magnetic electrode particles. The stationary working electrode, which served as the current source for the electrode particles, had a surface area of 4  $\text{cm}^2$  and consisted of an expanded metal disc and a wire as current lead. A silver-silver chloride reference electrode was used for all experiments with this type of reactor. The reference electrode had a distance of 10.5 mm from the wire of the stationary working electrode and 20 mm from the expanded metal disc. If the working electrode surface was enlarged by means of electrode particles, the reference electrode had a radial distance of 3 mm from the particle bed. To ensure that the electrode particles did not come into contact with the reference electrode, a PTFE filter with a mesh size of 6  $\mu\text{m}$  was installed in front of the reference electrode. For better flow distribution, a bed of glass beads was installed in front of the entrance of the two electrode chambers. The glass beads had a diameter of 2 mm. A more detailed description of the reaction system has already been published in the paper [14].

To evaluate the effect of the suspended non-conducting particles on the conductivity of the fluidized bed electrode, another fluidized bed reactor having only one reaction chamber was developed (see Fig. 2B). Here, the electrical resistance of the fluidized bed electrode could be measured between the working and counter electrodes. As a result, the working and counter electrodes were localized in the reaction chamber

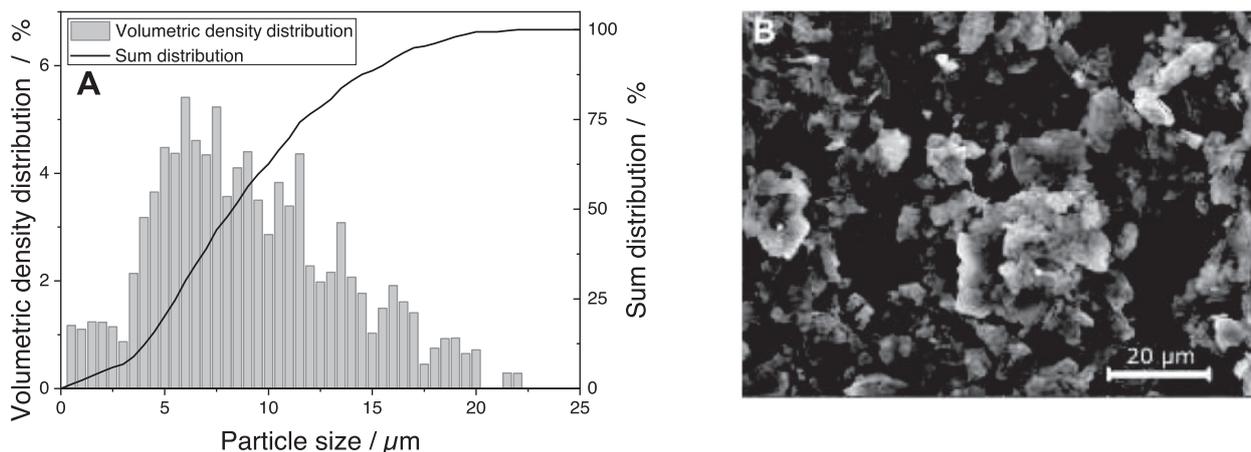


Fig. 1. A: Volumetric density distribution of the particle size of Amberger-Kaolin. Based on the volume distribution the mean particle size is 8.5  $\mu\text{m}$ . B: Electron microscopy image of Amberger-Kaolin. The particles show a broad distribution of the volumetric particle size distribution from approximately 3.8 to 15.5  $\mu\text{m}$ .

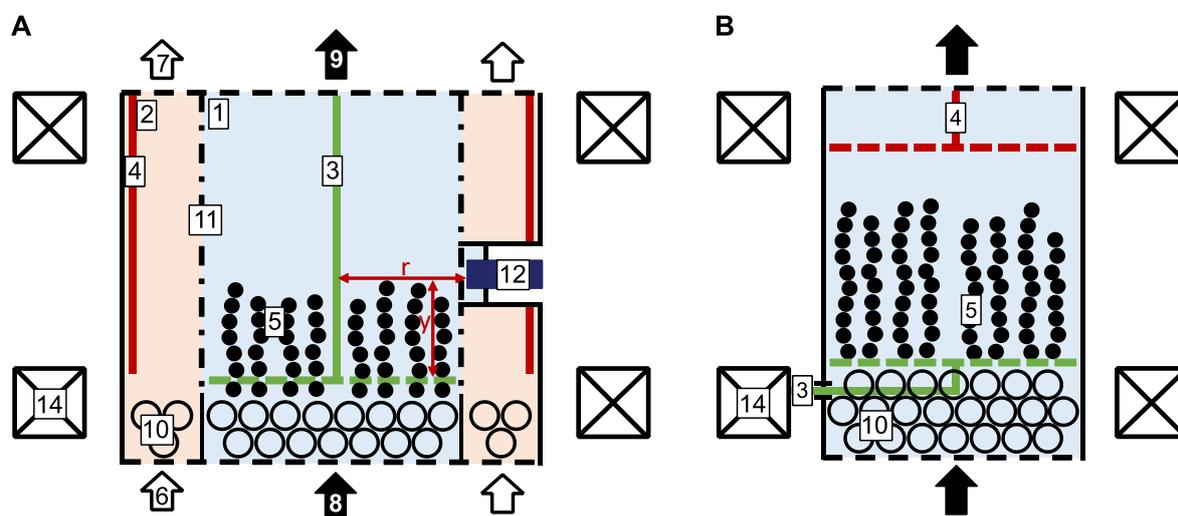


Fig. 2. A: Schematic illustration of the fluidized bed reactor to investigate the electrochemical conversion (modified from [14]); B: Schematic illustration of the fluidized bed reactor to investigate the conductivity of the fluidized bed electrode (modified from [10]); 1: working electrode chamber; 2: counter electrode chamber; 3: stationary working electrode = current collector. The working electrode consisted of an expanded metal disc and a wire with a thickness of 1 mm; 4: counter electrode; 5: magnetic electrode particles; 6: inflow direction of the counter electrode chamber; 7: outflow direction of the counter electrode chamber; 8: inflow direction of the working electrode chamber; 9: outflow direction of the working electrode chamber; 10: glass beads; 11: cation exchange membrane; 12: silver-silver chloride reference electrode: The reference electrode was positioned with a radial distance  $r$  of 10.5 mm from the central wire and a height  $y$  of 20 mm from the expanded metal disc forming the stationary working electrode; 14: electric coil for generating the magnetic field.

(19 mm inner diameter and 10 cm length). The working and counter electrodes had the same dimensions with an electrode surface area of 4  $\text{cm}^2$  and were made of platinumized titanium. The two electrodes were fabricated from an expanded metal disc and a wire, which was welded to the disc. The counter electrode could be freely positioned within the reaction chamber depending on the experimental conditions. The specific resistance of the particle bed could be calculated via the distance of the two electrodes. A more detailed description of the reaction system can be found in [10].

Within the working electrode chamber respectively the reaction chamber, the magnetic electrode particles could be influenced by a magnetic field. For this, a Helmholtz coil was placed around the reaction system. Using the Helmholtz coil, DC magnetic flux densities from 0 to 20 mT were generated in co-flow direction. During the whole process the coils were cooled. The generated magnetic fields were verified by means of a Hall probe. The Hall probe was mounted on a FH 31 Gaussmeter from Magnet-Physik Steingroever GmbH (Cologne, Germany).

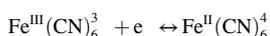
## 2.6. Experimental set-up

The fluidized bed reactor was connected to the pumps of a FPLC (Fast Protein Liquid Chromatography) system (Akta purifier 100, GE Healthcare, Buckinghamshire, UK). This allowed the flow rate to be set and controlled individually for the two electrode chambers. The electrochemical conversion was monitored by means of a redox electrode respectively ORP electrode. The redox electrode / ORP electrode allowed the redox potential of the continuously fed solution to be measured at the outlet of the reaction system. The redox potential was used to determine experimentally the electrochemical conversion of potassium ferricyanide to potassium ferrocyanide [14,27]. The solids-containing reaction solution was filled into a so-called Superloop (Superloop 150 mL, GE Healthcare, Buckinghamshire, UK), ensuring that the solids had no contact with the pump system of the FPLC system. The piston pumps used are not suitable for solutions containing solids. Therefore, a displacement principle is applied in which the pump pumps into a cylinder where two areas are separated from each other in a

liquid-tight arrangement by a movable stamp. In the lower area is the solid solution. By pumping an aqueous solution, the corresponding volume of solids-containing suspension is simultaneously transferred from the cylinder into the reactor. The reaction solution inside the Superloop was stirred during the reaction process in order to prevent a sedimentation of the solids. The potentiostat Interface 5000 from Gamry (Warminster, USA) was used to supply the required currents at a pre-defined potential of the working electrode in relation to the reference electrode. A schematic illustration of the experimental set-up is shown in Fig. 3.

## 2.7. Reactor operation

The investigations onto the electrochemical conversion were performed by means of a model redox reaction. As model redox reaction potassium ferricyanide and potassium ferrocyanide was used.



The oxidation of the 3 mM potassium ferrocyanide solution took place in the counter electrode chamber. The reduction of the 3 mM potassium ferricyanide solution was carried out in the working electrode chamber. In both solutions 1 M potassium chloride was used as a conducting salt. To investigate the influence of suspended, non-conducting solids onto the performance of a fluidized bed electrode, Amberger-Kaolin particles were added to the reaction solution entering the working electrode chamber. Furthermore, it should be mentioned that experiments on the size of the counter electrode have shown that it is large enough not to influence the current through the fluidized bed electrode during the electrochemical conversion experiments. The studies regarding the resistance of the fluidized bed electrode system with and without magnetic influence were performed with DC chronoamperometric measurements. To fluidize the electrode particles, a 1 M sodium chloride solution was pumped through the reaction system. Also in this experimental procedure, Amberger Kaolin was added to the electrolyte solution to investigate the influence of a solid-containing feed solution. Before each experiment, the solutions were gassed with nitrogen in order to strip oxygen. In addition, the high electrolyte concentration reduced the oxygen solubility [28].

### 2.7.1. Investigation of the electrochemical conversion

Chronoamperometric studies were applied to investigate the electrochemical conversion. To perform the chronoamperometric studies, two reaction solutions were prepared for the working and counter electrode chambers. In addition, Amberger Kaolin was added to the solution entering the working electrode chamber at different concentrations of 0, 1, 20, and 40 g/L, respectively. To perform the experiments, the reaction solutions were pumped through the fluidized bed reactor at a flow rate of 1 or 2 mL/min. The electrochemical conversion was studied at the potentials of 0.2, 0.4, 0.6, and 0.8 V adjusted by means of the reference electrode. The magnetic influence on the electrochemical conversion was studied at a magnetic field of 0 and 20 mT. The magnetic superposition of the fluidized bed electrode was performed in the "magnetization-last" mode. In the "magnetization-last" mode, the particle bed is superimposed with a magnetic field after fluidization is initiated [18,19]. The results of these experiments allowed the calculation of the electrochemical conversion as well as the effective electrode surface of the fluidized bed electrode. The calculation of the electrochemical conversion was performed as follows:

The electrochemical conversion (*Yield*) was calculated from the maximum possible current ( $I_{max}$ ), which can be generated during reduction of potassium ferricyanide and the actual measured current ( $I$ ) (see equation (2.1)).

$$Yield = \frac{I}{I_{max}} \cdot 100 \quad (2.1)$$

The maximum possible current was calculated using Faraday's law. Here,  $F$  stands for the Faraday constant,  $c$  for the molar concentration of the supplied solution,  $z$  for the number of transferred electrons in the redox reaction and  $\dot{V}$  for the volume throughput.

$$I_{max} = \dot{V} \cdot c \cdot F \cdot z \quad (2.2)$$

The calculation of the effective electrode surface was performed as follows:

The effective electrode surface ( $A$ ) was calculated according to equation (2.3). Here,  $(\epsilon)$  represents the bed porosity,  $(\beta)$  the mass transfer coefficient and  $(c_0)$  for the inlet concentration [14].

$$A = \frac{\dot{V}}{\epsilon \cdot \beta} \cdot \ln \frac{c}{c_0} \quad (2.3)$$

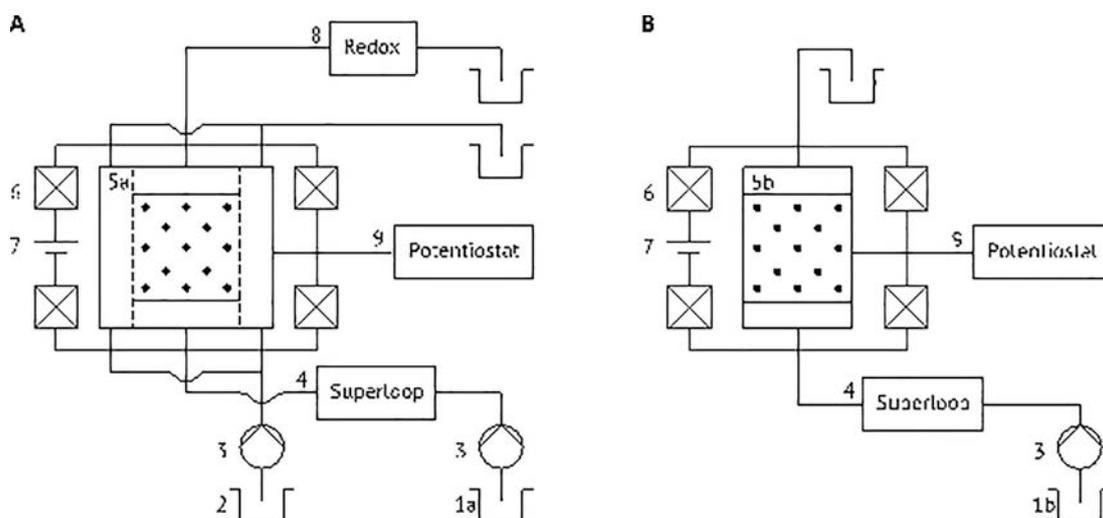


Fig. 3. A: Set-up of the reaction system for the electrochemical characterization; B: Set-up of the reaction system for the investigation of the conductivity of the fluidized bed electrode; 1a and 1b: water reservoir for the Superloop; 2: reservoir of the counter electrode solution; 3: pulsation-free piston pump system for the electrode chambers; FPLC-System (Äkta purifier 100, GE Healthcare, Buckinghamshire, UK); 4: Superloop: reservoir of the reaction solution respectively of the electrolyte solution; 5a: electrochemical fluidized bed reactor with two reaction chambers; 5b: electrochemical fluidized bed reactor with one reaction chamber; 6: Helmholtz coil; 7: direct current source for the Helmholtz coil (RND 320-KA3005D, Distrelec Group AG, Nänikon, Switzerland); 8: unit for measuring the redox potential; 9: potentiostat: (Interface 5000, Gamry, Warminster; USA).

The concentration ratio between the inlet  $c_0$  and outlet concentration was calculated according to equation (2.4).

$$\frac{c}{c_0} = \frac{I_{max} - I}{I_{max}} \quad (2.4)$$

The mass transfer coefficient was calculated using the Sherwood number, the diffusion coefficient and the particle diameter of a single fluidized bed particle. The Sherwood number was calculated according to Pickett [29]. A more detailed description of the derivation and calculation can be found in [14].

### 2.7.2. Investigation of the conductivity of the fluidized bed electrode

In order to investigate the conductivity of the fluidized bed electrode, the ohmic resistance between the working and counter electrode was measured. Knowing the ohmic resistance  $R$ , the cross-section of the bed  $A_{cross}$ , and the distance between the two electrodes  $l$ , the specific resistance  $\rho$  of the electrode bed could be calculated (see equation (2.5)). The working and counter electrodes had the same dimensions and consisted of an expanded metal with a diameter of 18 mm. A wire with a diameter of 1 mm was welded to the center of the expanded metal. A constant potential was applied between the two electrodes and the resulting current was recorded for the potentials 0.4 and 0.6 V until a steady state was reached. With the chosen potential range, it was ensured that no side reactions would occur.

$$\rho = R \cdot \frac{A_{cross}}{l} \quad (2.5)$$

For the resistance measurements the counter electrode could be placed at different positions within the reaction chamber. The experimental procedure was carried out at a flow rate of 1 mL/min. Furthermore, all experiments were performed with an Amberger Kaolin concentration of 0 and 1 g/L to investigate the influence of the solid-containing reaction solution on the conductivity of the fluidized bed electrode. In addition, to investigate the influence of the magnetic stabilization, all experiments were performed with a magnetic superposition of the particle electrode with a magnetic field strength of 0 and 20 mT. The magnetic superposition of the fluidized bed electrode was performed in the "magnetization-last" mode [18,19].

## 3. Results and discussion

### 3.1. Influence of solid-containing reaction solutions

The influence of solid-containing reaction solutions on the electrochemical conversion as well as on the effective electrode surface was investigated at different solid concentrations of 0, 1, 20 and 40 g/L. Amberger-Kaolin was used as a solid, which can be regarded as electroinactive substance. In comparison to the electrode particles (mean particle size of 175  $\mu\text{m}$ ), the substance Kaolin had a much smaller mean volumetric particle size of 8.5  $\mu\text{m}$ , so that the solid can pass freely through the fluidized particle bed. The electrochemical reaction was investigated in the working electrode chamber, in which the electrode surface was enlarged by means of electrode particles. In previous investigations it was shown, that in case of the used fluidized-bed reactor, electrode particle masses larger than 3 g had no significant influence on the electrochemical conversion [14]. Here, electrode particle masses of 3 to 5 g were investigated, with the sedimented electrode particles occupying fractions of 45 to 69% of the total volume of the reaction chamber. In consequence, all experiments of this section are conducted with an electrode particle mass of 3 g for the fluidized bed electrode. In previous investigations, it could also be shown that the superposition of the fluidized bed electrode by a magnetic field leads to an improvement of the electrochemical conversion by enhancing the conductivity of the fluidized bed electrode [10,13,14]. In this work we investigate the effect of the superposition of a magnetic field in the presence of non-conductive particle suspensions. The results of the non-magnetically

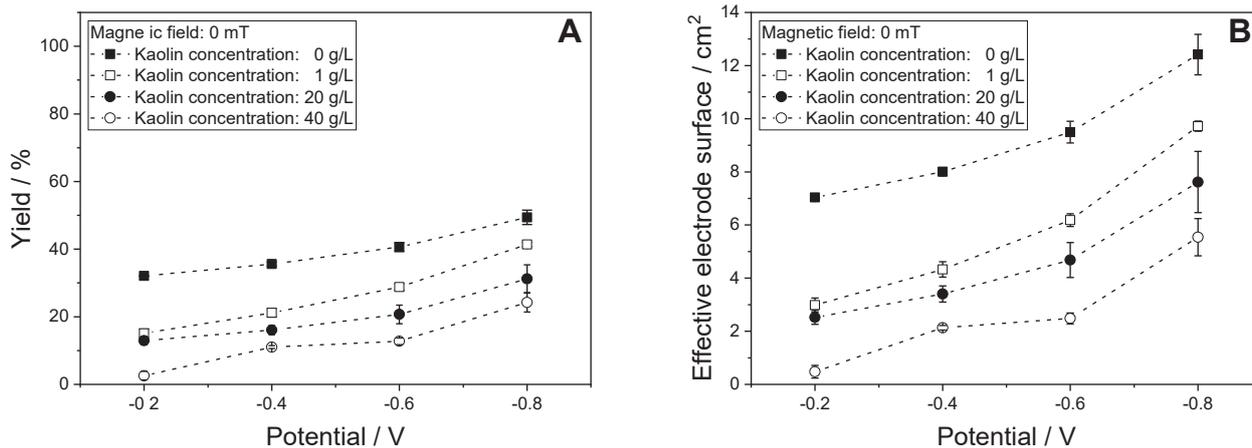
superimposed and the magnetically superimposed experiments are shown in Fig. 4 and Fig. 5. The expansion of the fluidized bed was 9% at a flow rate of 1 mL/min. With magnetic superposition of the fluidized bed electrode, the expansion was reduced to 6%.

#### 3.1.1. Particle electrode without superposition of a magnetic field

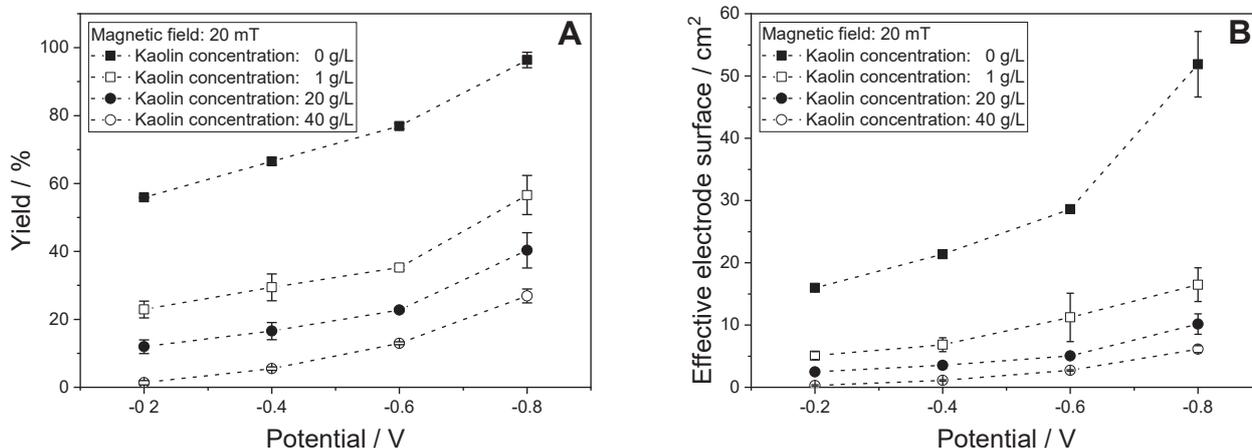
The results of the electrochemical reduction of a potassium ferricyanide solution using a fluidized bed electrode in presence of non-conductive particles are shown in Fig. 4. In order to focus the scope of this section, only the results of the fluidized bed electrode without superimposed magnetic field are discussed first. The resulting currents of the electrochemical reaction were determined in triplicates from three independent experiments. As can be seen, the experiments show a high reproducibility with a low standard deviation. As a benchmark for the influence of the presence of non-conductive solids in the fluidized bed, the electrochemical reaction was first evaluated with a solid-free reaction solution.

Considering the results in Fig. 4A, it can be seen that in the potential range from 0.2 to 0.8 V, the electrochemical conversion increases with decreasing potential. For example, at a flow rate of 1 mL/min, and at the potentials 0.2 and 0.6 V, an electrochemical conversion of 32 and 41%, respectively, can be determined. If the potential of 0.8 V is also considered, an electrochemical conversion of 49% can be calculated. With respect to the last example, it should be mentioned, that at a potential of 0.8 V, the occurrence of side reactions with the water species cannot be fully excluded. Consequently, the calculation of the electrochemical conversion of the ferricyanide reaction via the resulting currents somewhat overestimates the true values. In a previous work, it could be shown by measuring the true ferricyanide/ferrocyanide ratio using a redox electrode, that at a potential of 0.8 V the electrochemical conversion estimated via the currents were between 2 and 7% to high [14]. The highest deviation of 7% was found when an electrochemical conversion of more than 90% was reached. Based on these findings, it can be concluded that at 0.8 V the occurrence of side reactions is negligible in first approximation. Another important aspect is the behavior of the calculated electrochemical conversion in relation to the potential. If the potential difference between the working and reference electrode was increased, the determined electrochemical conversion was also increased. In the previous work, it could be shown that this potential dependence of the electrochemical reaction is caused by two main charge transport mechanisms within the fluidized bed electrode, the conductive and convective charge transport [10,14]. The conductive charge transport mechanism is based on the random formation of particle chains, forming a conductive path within the fluidized bed electrode [6]. The convective charge transport mechanism, on the other hand, is based on the fact that the electrode particles are charged capacitively in contact with a current source [11]. Afterwards, the charged particles can share their charge through random contact with other electrode particles within the electrode bed. Furthermore, it could be shown that a strong potential drop within the fluidized bed electrode is caused by the high ohmic resistance of the particle electrode. As a result, a larger fraction of the particles in the fluidized bed can be electrically charged at a potential of the working electrode of e.g. 0.8 V, compared to a potential of 0.6 V. The high ohmic resistance of the particle electrode influences the conductive and convective charge transport equally, so that only a small part of the particles of the particle electrode, located close to the current collector in form of a metal mesh, can participate in the electrochemical reaction due to the strong potential drop within the fluidized bed electrode.

Looking at the results obtained with a solids-containing reaction solution, the basic behavior is similar to that of a solid-free reaction solution (see Fig. 4). However, a difference can be found in the values of the achieved electrochemical conversion. For the investigated potential range of 0.2 to 0.8 V, the electrochemical yield decreases with increasing Kaolin concentrations of 0 to 40 g/L. Thus, for example, at a potential of 0.8 V and at solid concentrations of 1, 20 and 40 g/L, the



**Fig. 4.** Investigation of the influence of non-conductive solids on the electrochemical reduction of potassium ferricyanide in a fluidized bed electrode without the superposition of a magnetic field. (A) Achieved electrochemical conversion in dependence of the applied voltage, (B) Calculated effective electrode surfaces corresponding with the measured conversion yields. The test series was carried out at different solid concentrations (Amberger Kaolin) of 0, 1, 20 and 40 g/L, at a flow rate of 1 mL/min and at potentials of -0.2, -0.4, -0.6 and -0.8 V.; Electrolyte: 1 M KCl solution; Reference electrode: Ag-AgCl.



**Fig. 5.** Investigation of the influence of non-conductive solids on the electrochemical reduction of potassium ferricyanide in a fluidized bed electrode with the superposition of a magnetic field. (A) Achieved electrochemical conversion in dependence of the applied voltage, (B) Calculated effective electrode surfaces corresponding with the measured conversion yields. The test series was carried out at different solid concentrations (Amberger Kaolin) of 0, 1, 20 and 40 g/L, at a flow rate of 1 mL/min and at potentials of -0.2, -0.4, -0.6 and -0.8 V. The magnetic field strength of the superimposed magnetic field was kept constant at 20 mT. Electrolyte: 1 M KCl solution; Reference electrode: Ag-AgCl.

electrochemical yield is reduced from 49% for a solids-free reaction solution to 41%, 31% and 24%. The solids-containing reaction solution can pass freely through the fluidized bed electrode and does not lead to blocking of the system. Therefore, at first sight, the presence of solids within the reaction solution should not have any influence on the performance of a fluidized bed electrode, at least in case of the investigated low volume fractions of the solids. However, the results in Fig. 4A illustrate that a solid-containing reaction solution has a strong influence on the electrochemical conversion process. Already at a solid concentration of 1 g/L (-0.8 V) the electrochemical conversion is reduced by 16%. Looking at a solid concentration of 40 g/L, the behavior is even more pronounced. Here the electrochemical conversion is reduced by up to 51%. We assume that the non-conductive suspended particles affect the contacting of the electrode particles with each other, so that effectively a smaller fraction of the electrode particles participates in the electrochemical reaction.

The fraction of electrode particles participating in the electrochemical reaction can be estimated by calculating the effective electrode surface area. The calculation is based on the assumption that the applied potential difference is high enough to approach a concentration of zero

of the reacting educt species at the particle surface and therefore a maximum concentration gradient exists between the electrode and the surrounding reaction solution. Therefore, the calculated effective electrode surface can also be regarded as a minimum value. Fig. 4B shows the results of the calculated effective electrode surfaces, which are based on the results of Fig. 4A. The two figures show similar characteristics, however, due to the non-linear relationship between the electrochemical yield and the effective electrode surface, the positive slopes of the curves in Fig. 4B are more pronounced. In the test series with a solid concentration of 0 g/L and potentials of -0.2 and -0.8 V, effective electrode surfaces of 7 and 12.5 cm<sup>2</sup> can be calculated. If the solid concentration is increased to 1 g/L respectively 40 g/L, however, an effective electrode surface area of 3 and 10 cm<sup>2</sup> (-0.2 V), respectively 0.5 and 5.5 cm<sup>2</sup> (-0.8 V) can be determined. The values of the calculated effective electrode surfaces clearly illustrate that the non-conductive solid particles within the reaction solution have a lasting effect on the reaction process. On the one hand, the random particle chain formation is hindered by the solid particles, so that shorter particle chain lengths are formed within the fluidized bed electrode. As a result, a smaller proportion of the electrode bed is electrically charged. On the other

hand, the non-conductive solid particles may also influence the capacitive charge transport. The capacitive charge transport is based on the charge transfer through the random contact of charged and uncharged particles, which are in constant movement within the fluidized bed. However, if a thin layer of non-conductive particles forms between two colliding electrode particles the charge transfer is disabled. Ultimately, the presence of solid particles within the reaction solution at a potential of 0.8 V and a solid concentration of 1 g/L leads to a reduction of the effective electrode surface of 22%. In contrast, at a solid concentration of 40 g/L, the effective electrode surface is reduced to 55% of the initial value.

### 3.1.2. Particle electrode with superposition of a magnetic field

In addition to the test series in which the effect of a solid-containing reaction solution on a regular fluidized bed electrode was investigated, the influence of a solid-containing reaction solution on a magnetically stabilized fluidized bed electrode was also evaluated. For this purpose, the fluidized bed electrode was superimposed with a magnetic field of 20 mT, which was generated with a Helmholtz coil. To investigate the influence of the suspended solids, the complementary test conditions to the test series without magnetic superposition were applied. In addition, a test series without suspended solids was performed as a reference. A compilation of the results of the electrochemical conversion as well as the effective electrode surface at a potential of 0.8 V can be found in Table S1.1 in S.I.

Fig. 5A and B clearly illustrate the influence of the solid-containing reaction solution as well as the influence of the magnetic superposition on the electrochemical conversion and on the effective electrode surface of the reaction system. In the reference experiment, which was performed without suspended solids, an electrochemical conversion of up to 94% could be determined at a potential of 0.8 V. If Kaolin particles at concentrations of 1, 20 and 40 g/L were added at the same potential of 0.8 V, the electrochemical yield was reduced to 57, 40 and 27%. This clearly shows that also in the case of a magnetically stabilized fluidized bed electrode, the solid particles within the reaction system influence the electrochemical reaction process. On first view and considering the results of our previous work [10,14], one would have expected that the magnetic stabilization of the fluidized bed electrode improves the contacting of the individual electrode particles independent of the solid content in the reaction solution. Fig. 5B shows a different picture. As the concentration of solid particles in the reaction solution increases, the determined electrochemical yield is significantly reduced and does not retain a constant value.

The influence of the solid particles on the fluidized bed electrode becomes even more apparent when the effective electrode surface is considered, which is shown in Fig. 5B. If the reaction solution does not contain any suspended solids, an effective electrode surface of 50 cm<sup>2</sup> can be determined at a potential of 0.8 V. However, if the reaction solution is combined with a solid particle concentration of 1 g/L, the calculated effective electrode surface drops sharply to 16.5 cm<sup>2</sup>. This shows that even a solid concentration of 1 g/L has a significant effect on the charge transport mechanisms within the fluidized bed electrode, resulting in only 30% of the original electrode surface being used for the electrochemical conversion. An interesting aspect is also the comparison of the effective electrode surface with the total electrode surface of the fluidized bed electrode. The total electrode surface of the fluidized bed was calculated on the assumption that the electrode particles have a spherical shape, an average volumetric particle size of 175 μm and a particle density of 2000 kg/m<sup>3</sup>. At a particle mass of 3 g, a total electrode surface of 500 cm<sup>2</sup> is calculated from the mentioned parameters. This simple estimation shows that even in the best case of a solid-free reaction solution, a potential of 0.8 V and a magnetic field strength of 20 mT, only about 10% of the theoretically available total electrode surface is participating in the electrochemical reaction. The height of the fluidized bed is approximately 50 mm for the parameters mentioned. Therefore, the height of the electrochemically active section of the

fluidized bed calculates to approximately 5 mm.

If the same calculation is applied to the experiments with solid-containing reaction solutions, it shows that in the case of a magnetically stabilized fluidized bed electrode, the presence of Kaolin at concentrations of 1 and 40 g/L reduces the electrochemically active surface to only 3.3% respectively 1.2% of the theoretical total electrode surface. This corresponds with heights of the active section of the fluidized-bed electrode of 1.6 respectively 0.6 mm.

Another interesting aspect is the comparison of the results of the regular (see Fig. 4) and the magnetically stabilized fluid bed electrode (see Fig. 5). Comparing the electrochemical conversion, it is apparent that the magnetic superposition of the fluidized bed electrode can improve the electrochemical conversion up to 100% at a potential of

0.8 V in case of a solid-free reaction solution. A comparison of the electrochemical conversions of the solid-containing reaction solutions shows a different picture. As the concentration of solids within the reaction solution increases, the magnetic effect of improving the electrochemical conversion is reduced. In solid-containing reaction solutions with solids concentrations of 1, 20 and 40 g/L, the magnetic superposition improves the electrochemical conversion by just 38%, 30% and 12%. This effect is even more pronounced, looking at the calculated effective electrode surface. The magnetic effect on the fluidized bed electrode improves in the case of a potential of 0.8 V and a solid-free reaction solution the effective electrode surface by a factor of 4. With a solid-containing reaction solution of e.g. 1 g/L this factor is reduced to 1.7.

### 3.2. Conductivity of the fluidized bed electrode

In the previous sections it was found that a reaction solution containing non-conductive particles, influences the electrochemical conversion as well as the effective electrode surface of the reaction system. An explanation of this behavior can be provided by the main charge transport mechanisms, the conductive as well as the convective charge transport. The charge transport mechanisms within a regular fluidized bed electrode without suspended non-conductive solids has already been discussed in detail in our previous work [10]. The starting point was the consideration, that the fluidized bed electrode consists of two pseudo-continuous phases with different conductivities, the phase of the particle electrode and the phase of the electrolyte solution in which the particles are fluidized. This picture of a fluidized-bed electrode is based on the investigations of a porous electrode by Newman and Tobias [30]. In the system investigated here, the fluidized bed electrode also consists of the phase of the electrode particles and the electrolyte. The difference in the investigated system is, that a reaction solution containing non-conductive particles flows through the fluidized bed electrode. Although, these particles pass through the fluidized bed electrode, they influence the charge transport and thus the conductivity within the system. Therefore, it can be assumed that the non-conductive solid particles change the properties of the fluid phase only very slightly but have a stronger effect on the apparent resistance of the particle electrode, since the contacting of the individual electrode particles is affected.

In Fig. 4 it was shown that a regular fluidized bed electrode is influenced by the solid-containing reaction solution with respect to the electrochemical conversion and the effective electrode surface. This indicates that the non-conductive solid particles have a direct influence on the main charge transport mechanisms. The conductive charge transport describes the random particle chain formation within the fluidized bed electrode, which creates a conduction path between the current source and the contacting electrode particles. If non-conductive particles flow through the fluidized bed electrode, the randomly formed particle chains will probably be interrupted and large parts of the particle bed cannot be electrically charged. If, on the other hand, a magnetic field stabilizes the fluidized bed electrode, the conductive charge transport can be improved, since the electrode particles arrange

themselves along the magnetic field lines and support the particle chain formation (see Fig. 5). However, even with a magnetically stabilized fluidized bed electrode, the non-conductive solid particles show an influence on the effective electrode surface of the fluidized bed electrode. The fluidized bed is fluidized by the solids-containing reaction solution, whereby the non-conductive particles are evenly distributed within fluid phase. The magnetic superposition of the fluidized bed electrode causes the electrode particles to align along the magnetic field lines in presence of the non-conductive solids. However, because of their small size the non-conductive particles can be trapped between the much larger electrode particles and interrupt the conductive paths of the electrode. As a result, the effective particle chains become shorter and the fraction of the particle electrode contributing to the electrochemical reaction gets less. In section 3.1.2 the theoretical length of the particle chains within a magnetically stabilized fluidized bed electrode was estimated. Here it was shown, that without using a solid-containing reaction solution the formed particle chains have a length of 5 mm. In contrast, a solid-containing reaction solution with a concentration of 1 g/L reduces the particle chain length to approx. 1.6 mm.

The convective charge transport describes the capacitive charging of the electrode particles in contact with the current source, which charges the electrical double layer of the electrode particles [11]. As the electrode particles move into other regions of the fluidized bed, the particles can share their charge with uncharged particles and form a conduction path within the fluidized bed. In the presence of a solid-containing reaction solution, the probability increases that although two electrode particles get in close contact, the transfer of capacitive charge is blocked by a thin layer of non-conductive particles preventing a direct contact of the conductive bodies. A schematic illustration of the charge transport within a fluidized bed electrode in the presence of non-conductive solid particles is shown in Fig. 6.

### 3.2.1. Chronoamperometric investigations of the conductivity

Another tool to investigate the characteristics of fluidized-bed electrodes is by means of chronoamperometric measurements. By these, the conductivity within a fluidized bed electrode can be investigated in dependence of the distance between the counter and the working electrode. In previous measurements using a solid-free solution, it was possible to distinguish between two regions [10]. In Fig. 6, these two regions have been schematically outlined. Region I was located near the working electrode and was dominated by the conductive charge transport. This region stretches over a distance, corresponding to the maximum length of conductive particle chains of a few millimeters. Region II, however, corresponds to larger electrode distances, where the charge transfer can only take place by the convective mechanism. To get a better understanding of the influence of a solid-containing reaction solution on the conductivity of a magnetically stabilized respectively a regular fluidized bed electrode, analogous chronoamperometric investigations were performed.

To investigate the resistance behavior of a fluidized bed electrode, which is fluidized with a solid-containing reaction solution, DC voltage measurements were carried out between two electrodes [31]. For this purpose, a special reaction system was used in which the distance of the counter electrode to the working electrode could be variably adjusted. To be able to measure the conductivity, it had to be ensured that a conductive path between the working and counter electrode was possible and that no side reactions occurred during the measurements. A simple 1 M NaCl solution with a solid particle concentration of 1 g/L was used to measure the conductivity. Conductivity measurements were conducted with a plain 1 M NaCl solution with a solid particle concentration of 1 g/L. Possible redox reactions which could happen in case of applied potentials having a modulus above approx. 1.2 V would be water electrolysis and the reduction of dissolved oxygen. However, the applied potentials were well below this limit. However, in case of the

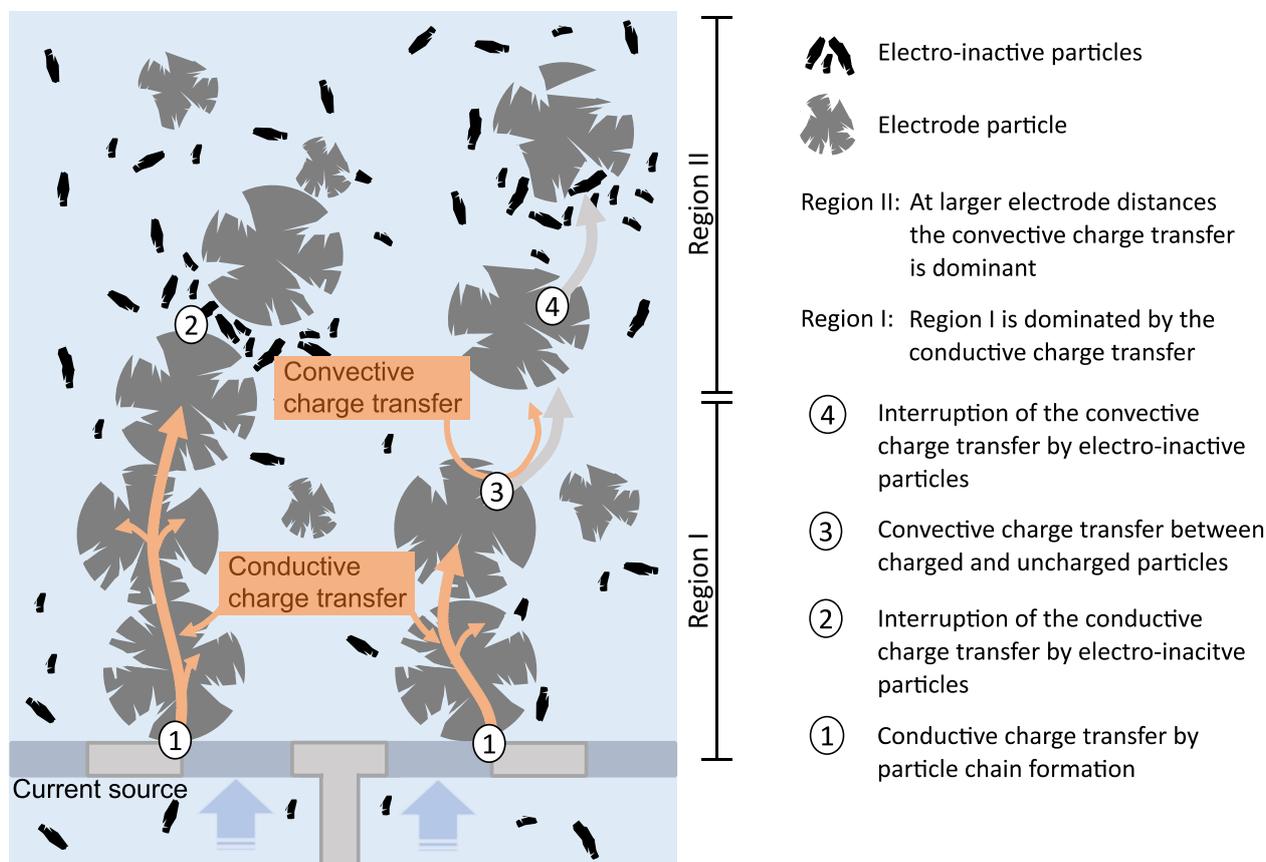


Fig. 6. Schematic illustration of the hindered charge transport within a fluidized bed electrode being passed by a suspension, which contains non-conductive solids.

applied potential differences between the working and counter electrode of 0.4 and 0.6 V these side reactions are neglectable. As in the previous sections, the non-conductive Kaolin particles were used as suspended solids in the reaction solution. In order to be able to compare the results of the conductivity measurement with the results of the electrochemical conversion, the conductivity measurements were also performed at a flow rate of 1 mL/min and with and without the superposition of the fluidized bed electrode by a magnetic field of 20 mT. The experiments including a test series without the addition of suspended solids were performed in triplicates.

For the obtained results, which are shown in Fig. 7, the counter electrode was positioned in the fluidized particle bed so that the resistance of the electrode bed could be determined as a function of the distance between the electrodes. The distance between the working and counter electrode could not be reduced below a value of 4 mm, although the counter electrode was carefully pressed against the working electrode in the fluidized state. In previous investigations it was assumed that at the smallest distance between working and counter electrode a thin layer of electrode particles is compressed. If, starting from the minimum distance, the distance between the two electrodes is stepwise increased, a region with low resistance values (100 to 200  $\Omega$ ) can be observed (region I). In a former work it could be shown that this region is dominated by the charge transfer along uninterrupted particle chains and allows direct electric conduction between the two electrodes [10]. Comparing the different experiments, which were performed with and without a solid-containing electrolyte solution, a difference in the determined length of region I is notable. In the presence of a solid-free electrolyte solution an extension of region I of up to 6 mm can be found. This value shows good agreement with the calculated length of 5 mm of the part of the fluidized bed, which effectively takes part in the electrochemical conversion (see section 3.1.2). Here, the extension of the length of the effective electrode was calculated on the basis of the determined electrochemical conversion rates and the effective electrode surfaces. If a solid-containing electrolyte solution with a concentration of 1 g/L was used for the fluidization of the particle electrode, low resistivities could only be determined in case of the minimum electrode distance of 4 mm. If this value is compared with the calculated extension of the electrochemically active part of the fluidized bed of 1.6 mm (see section 3.1.2), it shows that it is even smaller than 4 mm. We assume that this discrepancy is caused by slightly pressing the counter electrode in the direction of the working electrode in the resistivity measurements. By this, the electrode particles are artificially compressed at the smallest distance. In the regular fluidized particle electrode used in the experiments of section 3.1.2, the non-conductive Kaolin particles probably

interrupt the conductive chains of the particle electrode already at shorter particle chain lengths. For electrode distances greater than 4 mm (solid-containing electrolyte solution) or greater than 6 mm (solid-free electrolyte solution) the slope of the resistance curves changes dramatically. In region II, the convective charge transport dominates the charge transfer within the electrode bed. The resistance values show a linear ohmic behavior with increasing electrode distances. A constant slope can be determined for the resistance values with and without a solid-containing electrolyte solution as well as with and without magnetic superposition of the fluidized bed electrode.

To get a better overview of the influence of the solid-containing electrolyte solution as well as of the influence of the magnetic field, the specific resistivities were calculated (see Fig. 7B). Within the experimental errors, the resulting specific resistivities are constant values, independent of the electrode distance, but depending on the solid content of the electrolyte solution and the applied magnetic field. Looking at the average resistivity values, it is evident that the specific resistivity of the fluidized bed electrode increases in the presence of the non-conductive solid particles. For a solid-containing electrolyte solution with a concentration of 1 g/L, the resistivity increases from 336 (solid concentration: 0 g/L) to 385  $\Omega\text{m}$ . However, if the fluidized bed electrode is superimposed with a magnetic field of 20 mT, the specific resistivity can be reduced to 347  $\Omega\text{m}$ , corresponding to a moderate improvement of approx. 10%. In contrast, if a solid-free electrolyte solution flows through the fluidized bed electrode, the specific resistivity of the bed electrode can be improved under the influence of a magnetic field of 20 mT by 15%.

In summary, the chronoamperometric investigations showed that the effective length of the particle chains in region I of the fluidized bed electrode is strongly reduced by the non-conductive solid particles. The non-conductive solid particles interrupt the conduction path within the electrode particle chains, resulting in a particle chain length of less than 4 mm at a solid concentration of 1 g/L. Without a solid-containing electrolyte solution, however, particle chain lengths of up to 6 mm can be achieved. Region II of the fluidized bed electrode, in contrast, shows a very high specific resistance, which causes a strong potential drop within the fluidized bed. This allows mainly region I of the fluidized bed electrode to participate in the electrochemical reaction. However, by conductivity measurements it could be shown that the non-conductive particles also increase the specific resistivity in region II, however, only moderately.

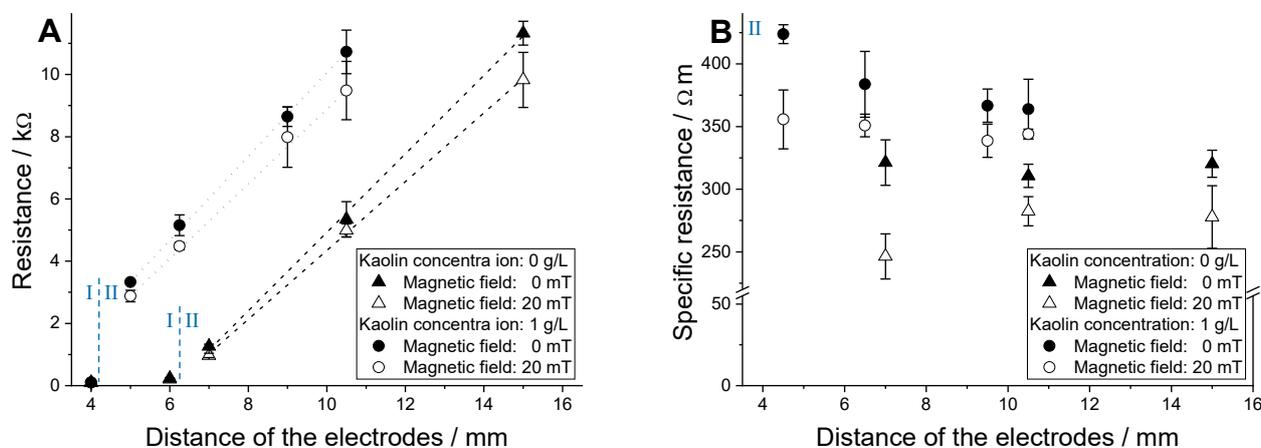


Fig. 7. A: Ohmic resistance within a fluidized bed electrode fluidized by a solution containing suspended non-conductive particles. The resistance was determined with and without superimposed magnetic field at varying distances of the electrodes. The resistance curves show two clearly distinguishable regions. Region I, valid for small electrode distances, shows small and only slightly increasing resistances. Region II, representing larger electrode distances, shows a strong but constant slope of the resistance values. B: Specific resistance of the fluidized bed electrode determined for region II; Flow rate: 1 mL/min; Magnetic field: 0 and 20 mT.

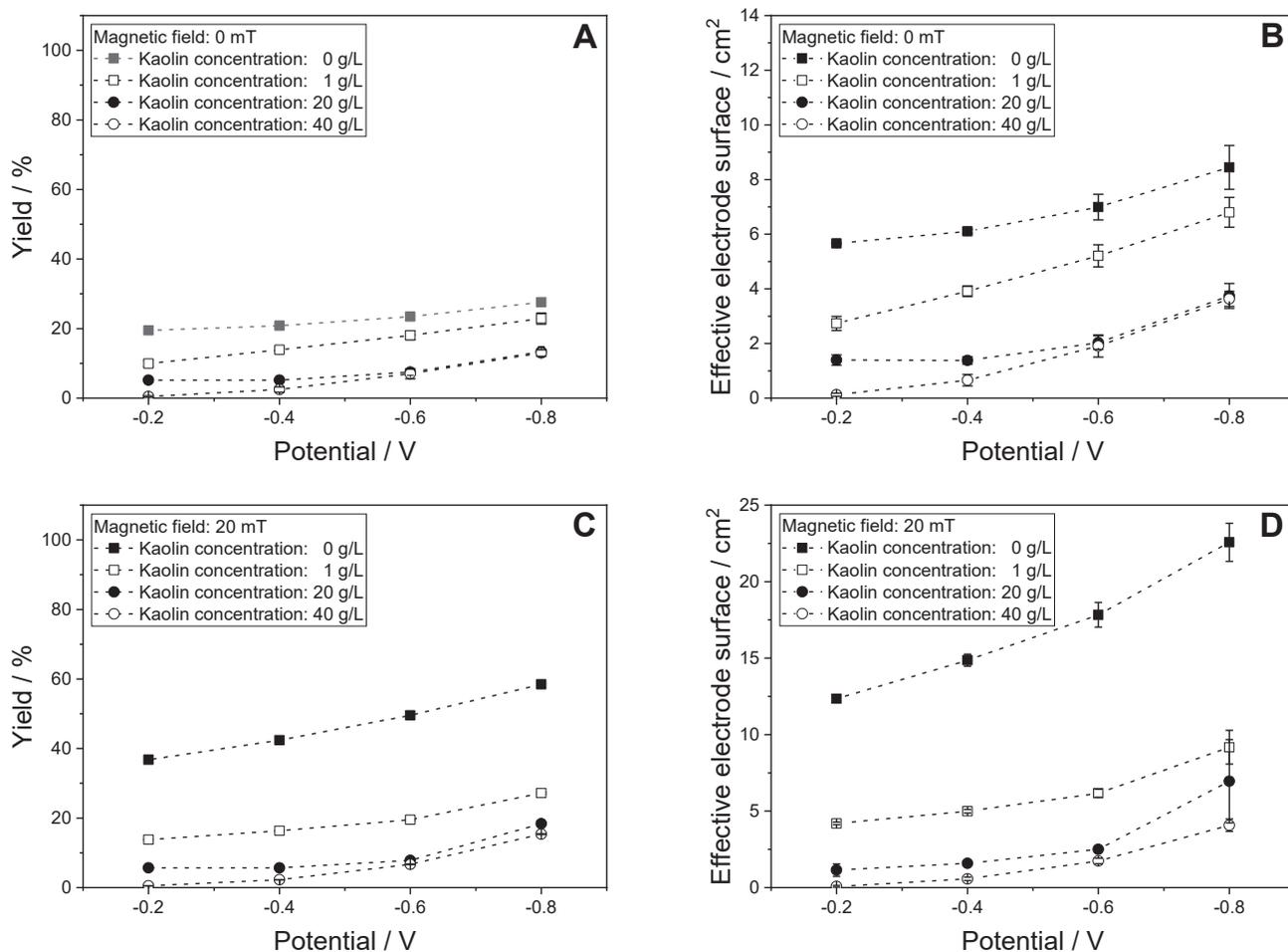
### 3.3. Influence of the flow rate

In this test series the influence of the flow rate on the electrochemical reaction with and without the use of a solid-containing reaction solution was examined. For this purpose, a flow rate of 2 mL/min was used instead of 1 mL/min. Except for the higher flow rate, the same parameters were used as in the previous experiments. For this purpose, reaction solutions with solid concentrations of 0, 1, 20 and 40 g/L were used for the reaction process. The magnetic influence on the fluidized bed electrode was also examined here with the magnetic field strengths of 0 (expansion of the fluidized bed: 17%) and 20 mT (expansion of the fluidized bed: 13%). The reduction of the 3 mM potassium ferricyanide solution, which was performed in the working electrode chamber, was carried out at the potentials of -0.2, -0.4, -0.6 and -0.8 V. The potential was adjusted between the working and reference electrode. In all test series the mass of the electrode particles was 3 g.

Fig. 8 shows similar courses of the yield and the effective electrode surface as the experiments conducted at a flow rate of 1 mL/min (see Fig. 4 and Fig. 5). The highest electrochemical yields in the investigated potential range can be achieved with a solid-free reaction solution. If the reaction solution contains non-conductive particles, the electrochemical yield decreases. In the case of a regular fluidized bed electrode without the application of an external magnetic field, an electrochemical conversion of up to 28% can be achieved using a solids-free reaction solution and a potential of -0.8 V. In contrast, if a solid-containing reaction

solution with a solid concentration of 40 g/L is used, the electrochemical conversion is reduced to approximately 13%. If a magnetic field of 20 mT is superimposed on the fluidized bed electrode, the electrochemical yield can be increased at solids concentrations of 0 respectively 40 g/L to 58 respectively 15%, showing again that the effect of a magnetic field is clearly reduced in the presence of suspended, nonconductive solids.

Furthermore, if the results presented are compared with the results of the experimental runs at a flow rate of 1 mL/min, it can be seen that the electrochemical conversion decreases with a higher flow rate. For the case of a regular fluidized bed electrode, at a potential of -0.8 V and a flow rate of 1 mL/min, an electrochemical conversion of up to 49% can be determined with a solid-free reaction solution. At a flow rate of 2 mL/min, this value is reduced to 28%. This behavior is caused by the fact that the fluidized bed expands more strongly due to the higher flow rate and thus the contacting of the electrode particles with each other deteriorates. Consequently, the higher flow rate reduces the active area of the particle electrode. Furthermore, the results show that the use of a solid-containing reaction solution at both flow rates reduces the effective electrode surface due to the presence of non-conductive, suspended solid particles within the fluidized bed electrode. As a result, at a flow rate of 2 mL/min, a potential of -0.8 V and a Kaolin concentration of 1 g/L, an electrochemical conversion of up to 23% can be achieved. At a flow rate of 1 mL/min, a value of 41% could be determined. Ultimately, the influence of a higher flow rate in the case of reaction solutions containing solids causes a reduction in the active area of the electrode



**Fig. 8.** Investigation of the influence of solid-containing reaction solutions on a magnetically superimposed and non-superimposed fluidized bed electrode based on the electrochemical conversion and the effective electrode surface: The test series was carried out at different solid concentrations of 0, 1, 20 and 40 g/L, at a flow rate of 2 mL/min, at the potentials -0.2, -0.4, -0.6 and -0.8 V and at magnetic field strengths of 0 and 20 mT. Amberger Kaolin, which has electro-inactive and non-conductive properties, was used as suspended solid in the feed stream; Electrolyte: 1 M KCl; Reference electrode: Ag-AgCl; Magnetic field: A-B: 0 mT; C-D: 20 mT.

surface.

#### 4. Summary and conclusion

In this study the influence of non-conductive suspended solids within the feed solution of an electrochemical reaction was investigated. The working electrode of the electrochemical reactor consisted of a particle electrode which could be superimposed by an external magnetic field. Amberger Kaolin with an average volumetric particle size of 8.5  $\mu\text{m}$  was used as solid substance, having non-conductive and electrochemically inert properties. By using a fluidized bed electrode for the electrochemical reaction the suspended solids could freely pass through the reactor without any signs of accumulation or blockage. However, the suspended, non-conductive solids showed a negative effect on the effectiveness of the electrochemical process. The superposition of an external magnetic field was able to improve the achieved yields by increasing the length of conductive chains within the fluidized particle electrode. However, even the magnetic stabilization could not prevent the negative influence of suspended non-conductive solids. Compared to the conversion yield obtained in case of a solid-free reaction solution at 20 mT, the electrochemical conversion yield was reduced from 92% to 56% applying a solution containing 1 g/L Kaolin at the same magnetic field and at a flow rate of 1 mL/min. At higher Kaolin concentrations the negative effect increases only moderate, reaching 26% at 40 g/L. Despite their reduced efficiency, fluidized particle electrodes are capable of successfully carrying out electrochemical reactions in reaction solutions containing a high solid content of non-conductive, inert particles. In contrast to packed bed or monolithic particle electrodes, which tend to block at high solid concentrations, fluidized bed electrodes offer the possibility to combine the advantages of a high specific electrode surface with a high tolerance to suspended solids. This combination makes fluidized bed electrodes particularly interesting for electro-biotechnological reactors, where electrochemical reactions are performed in the presence of high cell concentrations. Even though Kaolin (2600 kg/m<sup>3</sup>) has a different density like cell concentrations such as microorganisms (approx. 1050 kg/m<sup>3</sup>), there are similarities in the conductivity. Furthermore, the lower density of suspended cells would lead to a simplified discharge from the reaction system, so that the electrochemical conversion is not disturbed to a greater extent in this system either.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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