

EDITORIAL

This newsletter issue will focus on the achievements reached within the framework of the IMPULSE project in the field of electrochemical alkoxylation.

IMPULSE research in electrochemical alkoxylation goes beyond the mere application of microstructured systems in classical chemical technologies. So far, electrochemical technologies were not discussed intensively in the scope of multiscale process design. Nevertheless, in many applications electrochemical approaches have proven to be superior. This is especially the case in the areas of oxidation and reduction processes, where highly sensitive control of oxidizing and reducing power is crucial and can be easily controlled by the appropriate setting of the electrode potential. Industrial electrochemical processes that were originally found mainly in metal, chlorine and caustic production have now penetrated a broader spectrum of applications, including electrochemical synthesis.

Microstructured components have revolutionized electroanalytical techniques, but have not so far been considered from the point of view of electrochemical technologies. It is therefore a major aim of this part of IMPULSE research and development activities to prove the benefits of electrochemical technology within the philosophy of multiscale process design. This challenging multidisciplinary task requires extensive knowledge in the fields of electrochemistry, electrochemical and chemical engineering. Material science also plays a major role with respect to the durability of the material at process conditions and its suitability for apparatus manufacturing.

The IMPULSE developments in this area have yet to be proven against challenging industrial applications. Therefore, IMPULSE would like to offer to interested companies the opportunity for collaboration within the area of innovative electrochemical technology to demonstrate its industrial use. Please contact support team (supportteam@impulse-project.org) for further information.



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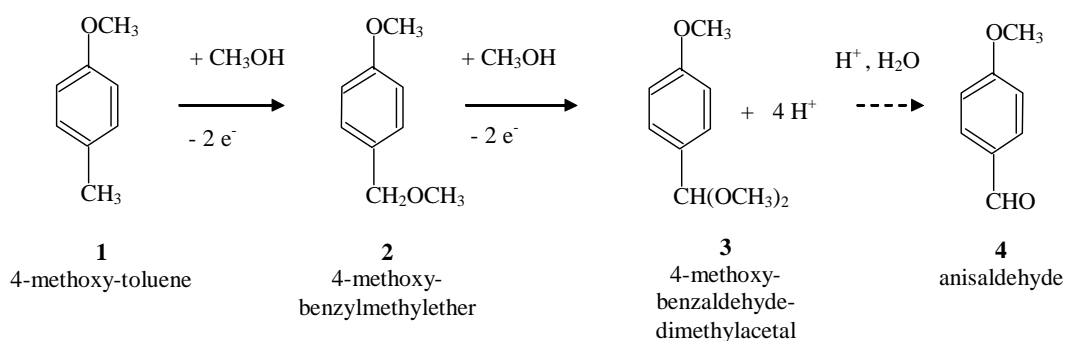
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Multiscale design in electrochemical synthesis - high conversion and selectivity single pass system

The issue of the microstructured electrochemical cell utilization for electrochemical synthesis was addressed together with detailed theoretical engineering characterization by Rode et al [1]. The results of this analysis form the basic idea of the IMPULSE research work in this area.

At first instance a suitable reaction system had to be selected. In agreement with the analysis provided by Rode et al. 4-methylanisole methoxylation was chosen. It can be described by the following reaction scheme:



Why electrochemical alkoxylation?

Introduction of an alkoxy group into the molecule structure is a very convenient way of the organic oxygen derivatives, such as the formation of ethers, aldehydes, ketons, esters etc. Specifically, 4-methoxybenzaldehyde (4-MBA) represents a high value compound. It is used in the production of numerous fine and specialty chemicals such as perfumes, dyes and drugs. Although there are elaborated chemical routes for production of this compound, the electrochemical approach represents the most promising one. This is mainly due to the very low selectivity of the oxidation step in the chemical routes. Electrochemistry is in a more favourable position. It allows for a simple and accurate reaction pathway (and thus selectivity) and reaction rate control by applying the electrode potential and current, respectively. Another important aspect is the industrial application of the selected reaction.

First generation electrochemical cell design

Design of a suitable microstructured cell represented the first important task. A narrow gap channel with a segmented anode made of glassy carbon was selected. This arrangement offers several advantages: A small electrode distance results in high conversion rate during a single-pass of the solution through the cell and a significantly reduced cell voltage because organic solutions are typically characterized by low conductivity. Furthermore, in the case of a strongly endothermic or exothermic process the solution can be efficiently tempered.

At the same time several questions remain unanswered. This concerns e.g. the impact of the anode segmentation on the homogeneity of the local potential and current density distribution on its surface due to the so called edge effect. Electrode reaction kinetics studies have been initiated to provide the relevant input data for mathematical modelling of the secondary current density distribution inside the cell. The results



were evaluated by Tafel kinetics and implemented into the model. An example of the calculated current density field is shown in Fig. 1. The influence of the interelectrode distance on the current density distribution along one half of the single anode segment in the middle of the channel is presented in more detail in Fig. 2. As documented by these results, reduction of the interelectrode distance is not only favourable from the point of view of the single pass high conversion, but also because of a significantly higher homogeneity of the anode current density distribution and thus improved process control.

On the other hand, a significant drawback of the interelectrode distance reduction is given by, beside significantly increased pressure drop in the electrolyte along the channel, the enhanced system sensitivity to the presence of the gas within this space. Since hydrogen

evolution represents the depolarization reaction taking place on the counter-electrode, this may represent an important issue. To minimize the influence of this aspect is one of the most important challenges of this task. A series of hydrodynamic cells was proposed and realized, allowing for the visualization of the flow inside the narrow gap channel with simultaneous gas evolution on the surface of the platinum electrodes localized at the electrolyte inlet to the cell. Results of this study clearly indicated the optimization nature of this task. Whereas high single-pass conversion is based on the relatively low electrolyte flow rate and high current density, prerequisites of the highly dispersed gas flow with a minimum impact on the homogeneity of the local current density distribution on the anode surface are just opposite.

The final design of the prototype cell used in the project was developed and realized by IMM within the first six month. It is shown in Fig. 3.

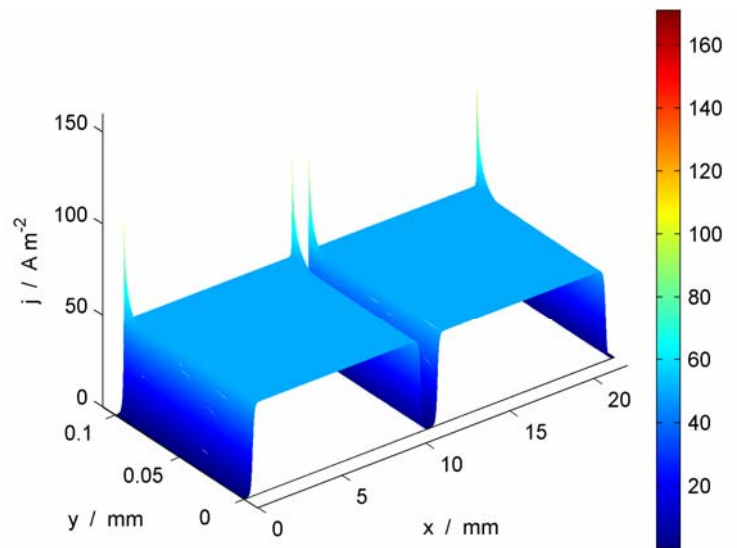


Figure 1: A typical example of the current density field inside the interelectrode gap for the average current density of 50 A m^{-2} .

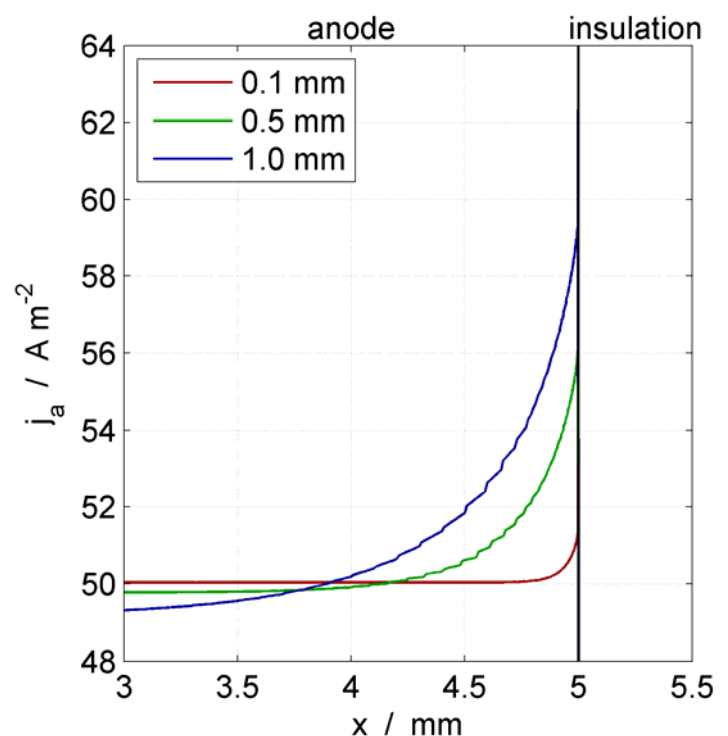


Figure 2: Influence of the interelectrode distance on the homogeneity of the local current density distribution along the anode segment surface.

Detailed system characterization

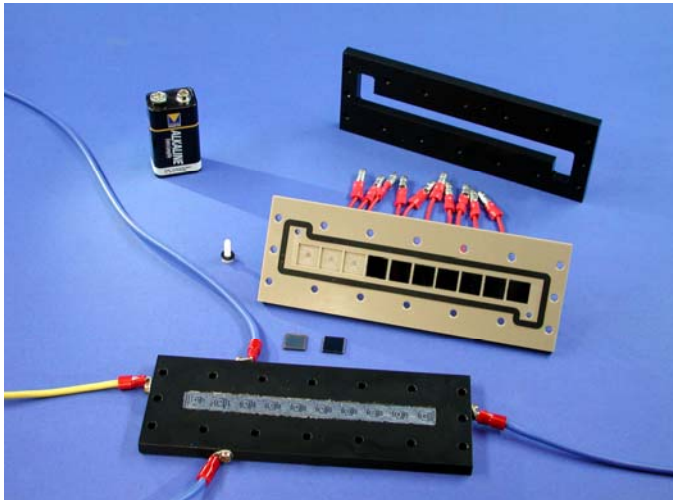


Figure 3: Photography of the first generation electrochemical cell.

Whereas the task to characterize selected processes in the microstructured cell fall into the responsibility of the CNRS/INPL group in Nancy, the remaining partners worked on a more detailed characterization of the entire system during this period of time. The electrochemical studies performed focused on two issues: anodic methoxylation pathway and the impact of the supporting electrolyte on it. A specific part of this study represents the evaluation of the potential of anodic methoxylation in an ionic liquids (ILs) environment. This study represents a highly innovative part of the IMPULSE project completed by ICTP in cooperation with Solvent Innovation. Utilization of ILs would have a positive impact on the safety of the

entire process. This is due to their non-flammability and zero partial pressure of their vapors. A second

benefit can be seen in the great variability of the IL molecular structure, which together with the expected unique structure of electrode double layer can lead to improved process selectivity. Series of ILs have been subject to screening for applicability. Finally, two ionic liquids have been selected and they will be subject of a more detailed study.

The study on the multiphase flow in the narrow gap channel formed by the interelectrode space was continued. New cells for the hydrodynamic studies have been designed and realized by ICPF, simulating closely the situation in the real electrolyser. Glassy carbon electrodes have been embedded into the carefully grinded glass walls. The construction of the cell is shown in Fig. 4. Typical examples of the flow patterns observed for different gas and liquid flow rates are shown in Fig. 5. Significant influence of both parameters, *i.e.* electrolyte flow rate and current density, on electrode surface accessibility for the electrochemical reaction is clearly evident.



Figure 4: Photography of the cell used for the visualization of the multiphase flow; left – glass channel with embedded glassy carbon electrodes, right – stainless steel framework.

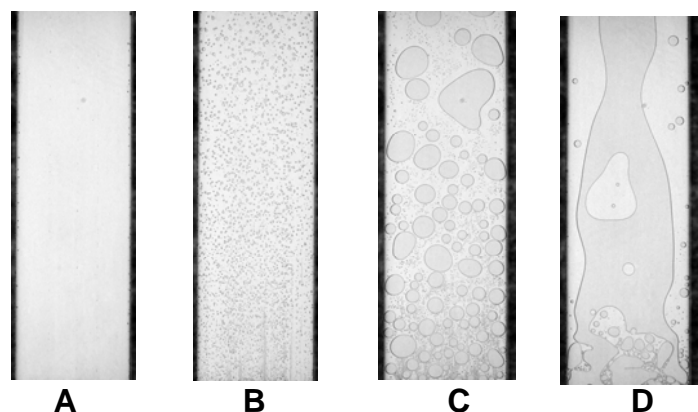


Figure 5: Typical flow patterns inside the narrow gap cell with electrochemically generated hydrogen;

A – no bubbles, $v_l=0.170 \text{ m s}^{-1}$, $v_g= 0.0048 \text{ m s}^{-1}$; B – dispersed bubbly flow, $v_l=0.170 \text{ m s}^{-1}$, $v_g= 0.0170 \text{ m s}^{-1}$; C – bubbly flow, $v_l=0.017 \text{ m s}^{-1}$, $v_g= 0.0170 \text{ m s}^{-1}$; D – churn flow, $v_l=0.017 \text{ m s}^{-1}$, $v_g= 0.0630 \text{ m s}^{-1}$.



Results of both, the first generation microstructured cell testing and the multiphase flow hydrodynamics, further stressed the importance of the gas accumulation in the electrolyte during its flow along the interelectrode channel. This is of a special importance in the case of intensive processes characterized by the high space-time yield and high degree of conversion. The studies provided indicate the necessity to separate at regular intervals gas from the reaction mixture. As an additional measure, increase in the operational pressure has been recommended. This approach is, however, limited by the increasing hydrogen solubility in the electrolyte mixture with the operational pressure. As a negative consequence of this aspect, the intensity of the parasitic reaction is enhanced, *i.e.* hydrogen oxidation on the anode. Pressure increase has thus to be considered carefully.

Second generation electrochemical cell design

The knowledge gained during this project phase has been utilized to propose the design of a second generation cell. The attention has been mainly paid to the additional two requirements given above, *i.e.* high cell throughput and elimination of the negative influence of the produced gas.

As another promising option, a bipolar electrode arrangement was selected. An important question in such an arrangement represents the optimal cell geometry providing both optimal utilization of the electric current flowing through the system and homogeneous electrolyte solution distribution in the individual channels at the same time. This problem has been studied by the means of mathematical modelling.

We may summarise the above brief information as follows: during the first two years of the project an important part of its targets has been completed. As one of the main results, the proof of principle has to be mentioned. As it has been shown by a series of mathematical models, the miniaturization of the specific cell dimensions results in a significantly improved electrode reaction control. The gas evolution originating from the counter electrode depolarization reaction has been identified as a major challenge. Knowledge generated during the project has allowed to suggest a solution to this problem. Improved cell design has been proposed and the cell constructed, see Fig. 6. It is now subject of intensive research aiming its characterization and assessment of the benefits of the structured multiscale design in comparison to the classical approach.

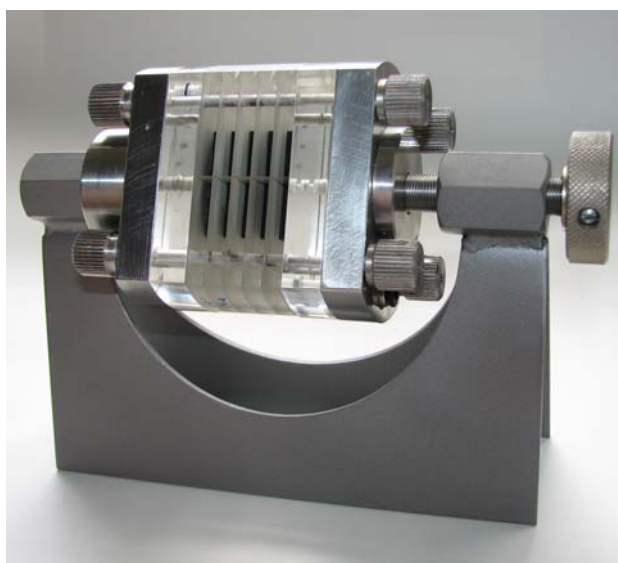


Figure 6: Microstructured bipolar reactor designed and realized within the project

Upcoming IMPULSE Events

The first meeting of the IMPULSE User Group, addressing equipment manufacturers and chemical end users, will be held in Frankfurt, Germany on 24 January 2008. IMPULSE representatives will introduce the methods of equipment characterisation and the equipment selection proforma. It is intended to discuss and validate the methodologies and to engage equipment manufacturers to facilitate a knowledge-based equipment selection for the application industries. The IMPULSE consortium believes this to be beneficial for both users and suppliers of process equipment. User Group participants are granted access to a password protected area on the IMPULSE website, in which the workshop material and additional IMPULSE information are available.

How to contact IMPULSE



Courtesy of IMM

To receive the biannual IMPULSE newsletter, please [subscribe here](#).

For joining the IMPULSE User Group, or questions and comments on the initiative, please contact the IMPULSE Support Team (SupportTeam@impulse-project.org) or visit our website at <http://www.impulse-project.org>, where we also announce presentations of IMPULSE research results at major conferences in the field of chemical engineering and chemistry.

