Proc. of the 1st Int. Conf. on Microreaction Technology,
Ed.: W. Ehrfeld. Springer Verlag, Berlin. 1998

Micro-Structure Electrodes as Electronic Interface between Solid and Gas Phase: Electrically Steerable Catalysts for Chemical Reactions in the Gas Phase*

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* Supported by the Ministerium für Wissenschaft und Kunst des Landes Hessen, FRG

Abstract. The application of **M**icro-**S**trip **E**lectrode (**MSE**) structures as electrically steerable catalysts to induce chemical reactions in gases is investigated. It can be shown that, depending on the geometry, the electric field strength, and the gas pressure in the MSE reactor, **chemical reactions can be 'switched on' and 'off' by applying a moderate voltage** (several 100 Volt). Due to the micro-structure dimensions already at these voltages electrons with mA/cm^2 current can be emitted from the solid to the gas phase without observable heating of the electrodes. The emitted and then accelerated electrons induce in an electrically steerable manner dissociation with subsequent chemical reactions via radical formation. Since a large number of final product molecules is generated per released electron, the MSE act as **dynamical catalysts**. The gas phase near the MSE surface contains two constituents: very hot electrons inducing molecular excitation and fragmentation, and rather cold radicals, molecular fragments, ions and gas molecules at a temperature externally selected for the synthesis process. The MSE reactor provides thus **a two-temperature system** at a wide pressure range, where the temperatures for molecular dissociation and synthesis can be chosen independently from each other. First stimulating results and possible areas of application are discussed.

1 Introduction

Plasma techniques are well established in chemistry and related areas of application [1], e.g. plasma arc processing of gaseous and liquid wastes or cleaning and edging of surfaces etc.. These non-thermal plasmas are created by differ-

ent processes, e.g. electrical discharges or electron beam irradiation. Since the basic plasma creation process proceeds via electron impact ionization, a plasma reactor must provide the following conditions:

1. A source for free electrons, i.e. electrons must be emitted from the solid electrode to the gas phase.
2. These electrons must be accelerated by the applied electric field $\vec{\mathcal{E}}$ over the free path length λ to gain the minimum kinetic energy E_{kin}:

$$E_{\mathrm{kin}} \;=\; \vec{\mathcal{E}} \cdot \lambda \quad > \quad E_{\mathrm{ex}}\,,$$

   where E_{ex} is the energy necessary for electronic excitation, fragmentation, or ionization of the gas molecules.

Condition 2 requires either a low gas pressure (vacuum conditions), i.e. large λ, or a very strong electric field. Typically for the creation and handling of electrical discharges with traditional techniques is therefore a low pressure environment and simultaneously high voltages between the macroscopic electrode structures. To fulfill condition 2 at normal pressure, where $\lambda \approx 1 \cdot 10^{-5}$ cm, $\mathcal{E}$ must exceed 10^6 V/cm which is very difficult to achieve with macroscopic electrode structures.

Electrode arrays fabricated on a micro-structure scale, however, can have sufficient small electrode dimensions that for moderate voltages (e.g. with 220 V AC) the created field exceeds the critical value E_{ex} and a discharge between the electrodes at 1 bar or even higher pressure can be produced. The mean field between the electrodes easily exceeds 10^5 V/cm and approaches 10^7 V/cm or even higher values near the edges of the electrodes. Thus MSE structures allow at normal pressure for DC discharges or short time avalanche discharges.

Therefore A. Oed [2] had the brilliant idea to use such structures as a new kind of position-sensitive discharge amplifiers to build new generation gaseous position-sensitive proportional counters and to replace the traditional multi-wire drift chamber devices [3]. In optimizing these micro-electrode devices (the so-called micro-strip detectors) for the use as gaseous proportional counters all internal discharge effects had to be eliminated. Thus in particular extremely clean chemical conditions in the detector had to be provided to avoid gas aging by chemical processes. Fighting this effect, a research group at Frankfurt university had the idea to use such structures to create electrically controlled large area discharges on MSE surfaces and to use them as a new kind of discharge reactor for chemical processes.

It is obvious that MSE structures easily provide the environment, to fulfill the above listened condition 2, i.e. $E_{\mathrm{kin}} > E_{\mathrm{ex}}$. But to build an efficient discharge reactor one needs also a source for free electrons in the gas phase (condition 1). Fortunately the MSE provides these electrons, too. If the gas pressure in the MSE reactor exceeds a few 10^{-2} mbar and a moderate voltage of a few 100 V is applied to the MSE, free electrons are immediately present in the gas phase and the discharge covers the whole MSE surface with a typical thickness of about 0.5 mm.

The MSE structures are thus acting as a new kind of electric interface between the solid and gas phase. They enable in a controlled manner the direct transfer of electric energy into kinetic energy of the free electrons in the gas phase. The kinetic energy is given by collisions between free-electrons and bound-electrons into electronic excitation of the gas atoms or molecules, and finally into a chemical reaction process. This transfer process can instantly be 'switched on/off' by turning on/off the electric field. Depending on the size of the electrode geometry large area as well as micro-scale discharges can be created with any time structure (nsec periods to DC). Because of the small size of the electrodes and because of the short distances the ions or radicals are drifting, the discharges follow immediately the applied voltage and provide a very fast interplay between solid and gas.

2 First MSE Test-Reactor

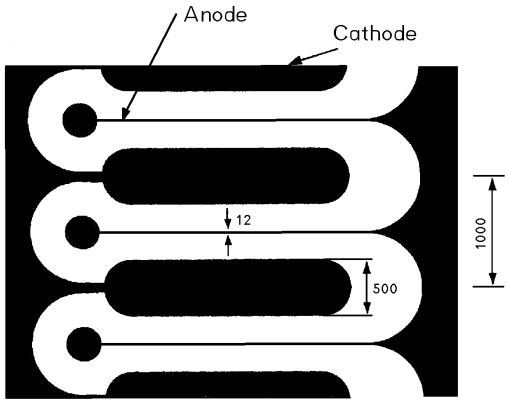

Fig. 1: Schematic presentation of the MSE layout used in the first test reactor. All values are in μm.

In Fig. 1 the geometry of the used micro-strip array is shown. This MSE structure was designed for controlled avalanche processes in proportional counters. The electrodes are made of thin gold strips evaporated on a glass bulk with a well chosen surface resistivity. The size of the used active MSE was about 3×3 cm^2. It contains edges (cathode) with a length of about 100 cm per cm^2. In Fig. 2 the schematics of the whole test reactor system including the diagnostics is presented. The test reactor made of stainless steel has a volume of about 1 liter. Because of diagnostic limitations only NO radicals could quantitatively be detected via the laser induced fluorescence technique. A laser

beam passed the reactor a few millimeter above the MSE surface and excites the NO molecules from the $X^2\Pi$-groundstate to the B-state. The fluorescence light emitted by NO molecules was detected under 90° by a photomultiplier sitting outside the reactor. The detected fluorescence light intensity was recorded and displayed on a PC system. Because of the large light absorption cross section

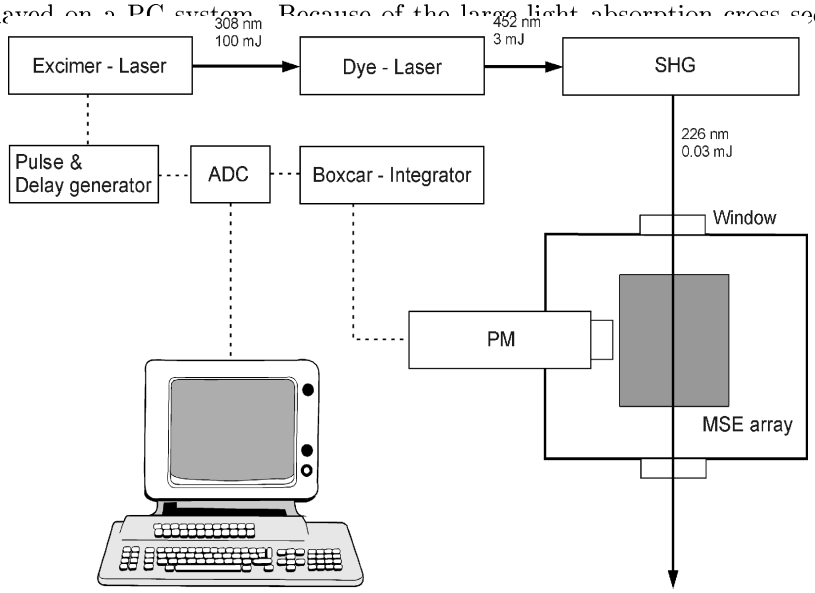

Fig. 2: Schematic presentation of the test reactor and the product analysis

this diagnostics technique works only for gas pressures below a few mbar. From the fluorescence light intensity the absolute NO concentration could be determined by calibrating the system with a pure NO gas filling. From the rotational spectrum and the width of the absorption line the NO gas temperature could be measured. The reactor was evacuated before each measurement and filled with the reaction gas mixture. During the measurement no additional gas was filled in or pumped out. Thus, gas exchange within the reactor could only proceed via normal diffusion processes.

3 First Results and Discussion

In Fig. 3 the formation of NO radicals is shown for a mixture of N_2 and O_2. It can be seen that by switching on/off the MSE voltage the formation of NO can instantly be induced. Since the laser detects only NO molecules just above the MSE surface the detected NO contribution does not remain constant but decreases immediately after switching off the voltage, since the formed NO molecules diffuse over the whole reactor volume. The measured time dependent NO contribution near the surface is proportional to the formation rate

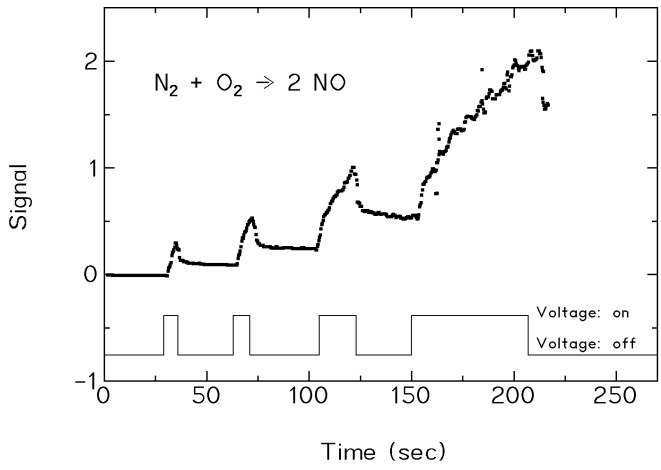

Fig. 3: NO synthesis with the MSE reactor

minus the diffusion rate. The analysis of the formation rate yields, that each free electron in the gas has created about 10 NO radicals. Thus about 40 eV electric energy are used for the formation of one NO radical. Varying the laser light frequency the absorption profile can be measured, which reflects mainly the doppler distribution. From this line width and also from the population of the monitored rotational states the NO temperature can be deduced. We find that the NO temperature remains close to room temperature.

In Fig. 4 the conversion of NO to N_2 and O_2 and the disintegration of N_2O to NO are shown. Again, one electron induces about 10 chemical reactions.

In further tests we could show that also CH_4 can be synthezised to higher organic compounds. For example, the *non-optimized* measured efficiency for synthezising (H−C≡C−H) from methane is nearly identical to those of optimal traditional plasma systems used for industrial production of acetylene.

Depending on the gas the MSE induced discharge emitts light at different colors. For Xe an intense blue light emission is observed. This light is emitted from a region just above the MSE surface.

These are just first tests of the new type discharge reactor based on MSE. Since for financial reasons we could only perform test measurements with such MSE which were originally produced for micro-strip detectors, the geometry and material of the available MSE could not be varied and optimized for the desired reactions. These first tests could only be used to prove the basic idea that these MSE can act like electrically steerable catalysts. Detailed investigations have to follow.

In particular, the mechanism of electron emission from the solid electrode into the gas phase is very little understood and one can only speculate about the

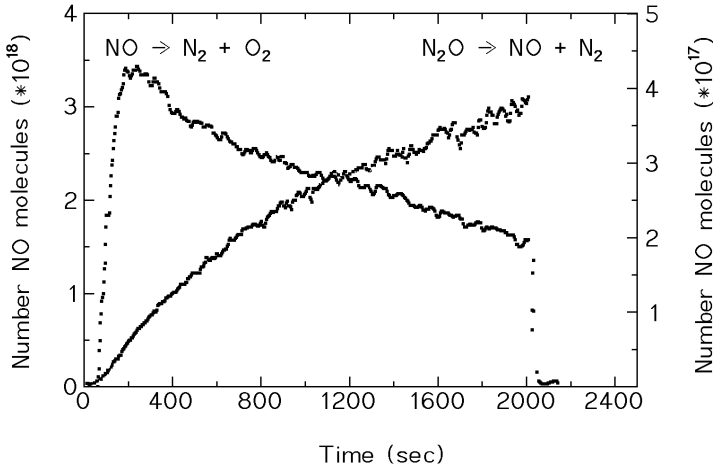

Fig. 4: NO conversion (left scale) and N_2O disintegration (right scale) with the MSE reactor

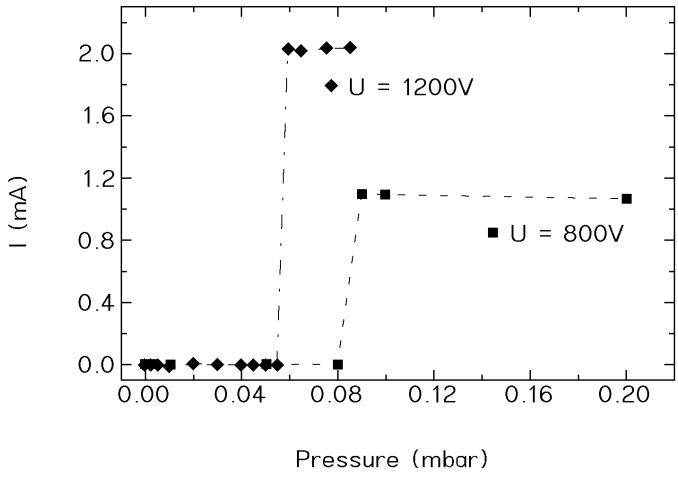

Fig. 5: Electron current as a function of the gas pressure

mechanism of cold electron emission by the MSE. As shown in Fig. 5 the electron emission depends strongly on the gas pressure in which the MSE are placed. At pressures below a few 10^{-2} mbar no measurable electron emission into the vacuum is seen. Then just above a critical value the electron emission increases exponentially reaching a saturation value. This critical pressure decreases with

increasing field strength. If the mechanism of electron emission would be pure field emission we should find some measurable current also at lower pressure. The sudden increase with pressure indicates that the scattering of molecules, radicals or ions on the sharp edges of the MSE induces the electron emission. According to [4] the gas constituents at the edge reduce the potential barrier for electron emission when they reach the solid edge. The electrons can tunnel via the potential well of the gas particle into the vacuum.

The MSE induced discharge should be quite different from a plasma like state. Due to the very small electrode distances the electric field penetrates the whole discharge regime. Thus, the electric and possible ionic flux can instantly be steered by the applied voltage. Furthermore the MSE discharge will not significantly heat the gas. Consequently, the MSE reactor provides a **two-temperature system**:

1. The electrons have mean kinetic energies equivalent to several 100.000 degree temperature. This electron temperature allows the dissociation and to a certain degree ionization of any molecule, e.g. even dioxin.

2. On the other side the gas, radicals or ions have average kinetic energies equivalent to room temperature.

The synthesis of the fragments or radicals will proceed at relatively low (room) temperature. Therefore, the temperatures for a two-step chemical reaction (e.g. generation of radicals via fragmentation and subsequent synthesis of new product molecules) can be chosen in a non-correlated manner and can be adjusted to the optimal temperature conditions for both reaction steps.This is quite impossible with the traditional plasma discharge devices.

With modern LIGA techniques even three-dimensional MSE (thin two-dimensional MSE are packed together to a multi-layer structure) can be produced. Instead of surface printed structures grid-like MSE structures [5] can be created, where the gas flows through several layers of MSE. Each layer can have another geometry or field strength. Thus, within 0.1 mm the field strength can drastically be varied and a large 'electronic' temperature gradient can be created over this distance. Such adjustment of temperature gradients in three-dimensional structures will shift the chemical reaction far away to non-equilibrium reaction dynamics and allow the formation of exotic components.

4 Applications

The new MSE allow the creation of large area discharge layers over a wide pressure range and also at normal pressure with very moderate voltages. Vacuum conditions are not crucial for the application. Therefore, the MSE can be used as electrically steered catalysts to synthezise quite inert gases and to reduce pollution and waste. Three-dimensional MSE with open channels (the gas can flow through) could be used as new kind of catalysts in the exhaust of automobiles, which can be activated just by applying a moderate voltage.

The MSE can be used at normal pressure for surface cleaning and edging even in the presence of rare gas. The electrically driven MSE would create excited rare gas atoms which have a huge chemical reaction potential which can break any bonding. Because of the very short distance between MSE surface and plasma treated object the excited atoms would react quite efficiently with the object surface. Depending on the gas mixture also layers of material could be deposited at normal pressure on the surface with controlled impact energy. Even new printers based on MSE could be developed.

Since the MSE can produce a very efficient large area light source (e.g. cold Xe lamps), it can be used as cold light emitters. Depending on the electrode geometry small micro discharges can be created and thus many micro light spots can be integrated to a large area display, where each spot can be switched on/off with very high speed. The MSE could provide a new kind of optical display. The thickness of the display would be much less than a millimeter and could have a spatial resolution in the few micron range.

Many other applications seem to be feasible. The electrically driven MSE is indeed a new electric interface between solid and gas phase. Everywhere this potential provides a new technological impact the MSE could open new windows of scientific or industrial applications.

Acknowledgement

We thank Dr. B. Willim and Dr. E. Dietz from the administration of the University Frankfurt for their great help in receiving the support by the Land Hessen. Furthermore, we thank Dr. V. Dangendorf who introduced to us the microstrip technique. Dr. H. Sann and Dr. J. Pochodzalla provided us with used microstrip structures. We are indebted for many helpful and stimulating discussions to Dr. Hiller (Robert Bosch GMBH), Prof. Kassing (Universität Kassel), Dr. Schmitt (IHK-Frankfurt), Dr. O. Schöller (Wissenstransferstelle der Universität Frankfurt) and many other collegues.

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