Surface charge tailoring for plasma catalysis

Robin Labenski(*)[1], David Steuer[1], Henrik van Impel[1], Marc Böke[2], Volker Schulz-von der Gathen[2], Judith Golda[1]

[1] *Research Group Plasma Interface Physics, Ruhr University Bochum, Bochum, Germany*
[2] *Chair Experimental Physics II, Ruhr University Bochum, Bochum, Germany*
(*) robin.labenski@rub.de

In photo- and electrocatalysis it is already well-established that surface charges can alter the chemical adsorption and reaction paths of the catalyst [1]. However, the novel realm of plasma catalysis lacks experimental exploration regarding the impact of plasma-induced surface charges on catalysis. So far, only a handful of theoretical density functional theory (DFT) calculations focusing on CO_2 splitting were carried out by the group surrounding Annemie Bogaerts. They suggest that negative plasma-generated surface charges can indeed lead to improved CO_2 activation resulting in higher conversion efficiencies [2–4].

Finding experimental methods to take a closer look at the relation between plasma-deposited surface charges and catalysis is therefore worth the effort. Our recent studies pave that way by presenting a new, yet simple method for precisely charging the dielectric (and eventually potential catalyst) using the plasma's ability to deposit surface charges. The charged dielectric is part of a Micro Cavity Plasma Array (MCPA) - a dielectric barrier discharge microplasma reactor introduced by Dzikowski et al. [5]. The method involves a relais circuit, with which the externally applied voltage $V(t)$ can be precisely shut off immediately extinguishing the plasma. This brings the surface charge deposition on the dielectric to a distinct halt and is shown in the left figure of Fig. 1.

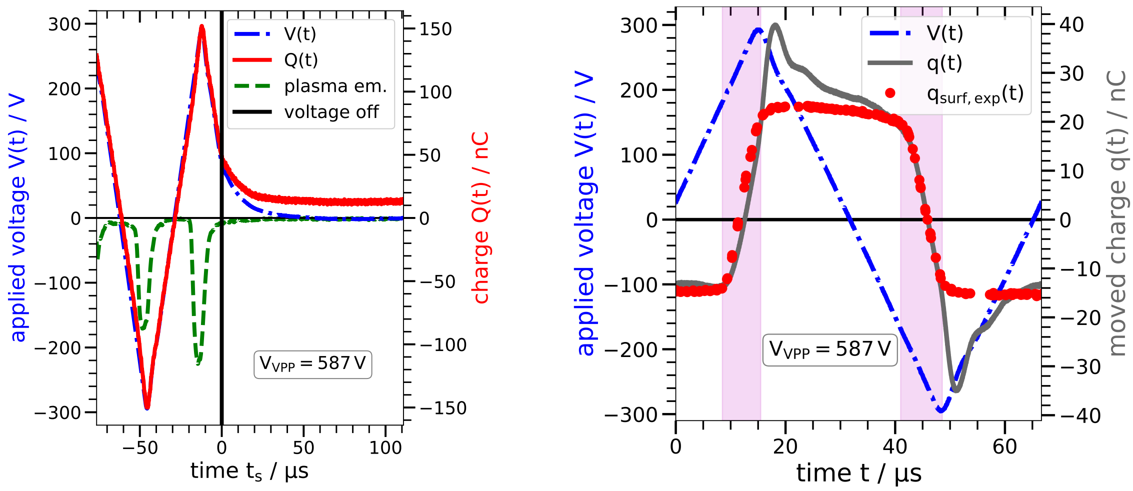

Fig. 1: Left figure: Switching of the relais circuit at $t_s = 0$ resulting in a shut off of the applied voltage $V(t)$ and revealing positive surface charges (positive offset in charge $Q(t)$). Right figure: Time-resolved comparison between the conventionally determined moved charge $q(t)$ and surface charge $q_{surf,exp}(t)$ utilizing the relais circuit. The pink highlights represent the discharge time frames. In both figures an excitation peak-to-peak voltage of $V_{VPP} = 587$ V at 15 kHz is applied.

Switching the relais at $t_s = 0$ results in a rapid decay of $V(t)$ revealing a (in that case) positive offset in the charge $Q(t)$. The latter is measured utilizing a monitor capacitor and corresponds to positive surface charge on the dielectric. By varying the moment in time the relais is switched the amount and polarity of surface charge can be precisely tuned. The time resolved amount of surface charge $q_{surf,exp}(t)$ on the dielectric is computable from charge $Q(t)$, when combined with a common equivalent circuit approach. Conventionally this only allows for the determination of moved charge $q(t)$ [6] containing surface charges, volume charges and potential artifacts. The addition of the relais circuit, however, enables a retrospective artifact- and volume charge-free determation of the actual surface charge $q_{\mathrm{surf,\,exp}}(t)$ during the discharge cycle as depcited in the right figure of Fig. 1.

The relais circuit is perfectly suitable for the charging of the dielectric, while also decoupling surface charges from the plasma. A manipulation of surface charge during an ongoing discharge is not possible though, as the switching of the relais results in the unavoidable shut down of the reactor. However, the introduction of a nanosecond laser allows for this *operando* manipulation of surface charge. As already found by Tschiersch et al., laser-induced electronic surface charge ablation of the pre-charged dielectric is possible, but the amount of ablated charge per pulse is small (order of $10\,\mathrm{pCcm}^{-2}$ in their case) [7]. A significant amount of surface charge in a comparably short time frame (few microseconds) could therefore be ablated by employing high repetition lasers.
A complementary laser-based method to accomplish a quick not decrease, but increase in surface charge is investigeated in our latest research. We find that with just a single nanosecond pulse (having the same wavelength of 532 nm and similar pulse energy in the order of 50 mJ as used by Tschiersch et al. [7]) an additional gain of surface charge of up to $15\,\%$ within $3.5\,\mu$s after irradiation and potential for even higher yields is achievable. The origin of these additional surface charges and their implication on the consecutive plasma cycle is also assessed.

References

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