Electrode erosion and possible effect on methylene blue degradation in a nanosecond pin-to-liquid discharge system

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Abstract: This work studies the erosion of high-voltage pin electrodes in nanosecond pulsed corona discharges above water. Different pin electrode materials (hafnium, copper, stainless steel) and gas atmospheres (oxygen, air) were used. In all cases, electrode erosion was observed. Moreover, the effect of the type of electrode on the degradation of a model organic pollutant, the dye methylene blue, was studied. Electrode erosion did not show any significant catalytic effect on the dye degradation.

Keywords: Plasma-activated water, pin-to-liquid, erosion, methylene blue.

1. Introduction

In the last years, plasma-activated water (PAW) has found an increasingly large number of applications in water purification, medicine, material synthesis and agriculture. [1]-[3] The interaction of non-equilibrium plasmas with liquid water produces a highly reactive environment that contains short-lives species including radicals and ions ('OH, NO', N2⁺, H2O⁺, etc.), longer-lived species (O3, H₂O₂, NO₂⁻, NO₃⁻, ONOO⁻), as well as UV radiation. [2], [4] In water purification applications, the reactive species of the PAW have shown promising results in degrading pollutants that are known to be difficult to treat with conventional water treatment technologies. [5] When testing new plasma-liquid reactors, dyes are typically used as model organic pollutants. [6] Dye degradation can be easily tracked, because the dye color fades in this process. Plasmachemical species attack the chromophoric groups of dyes, changing the absorption of the dye in the UV-vis region.[4]

Erosion of electrodes leads to challenges and opportunities in plasma-liquid applications. On the positive side, metals released into the water can enhance the removal of contaminants and microorganisms. [4], [7] One of the most studied reactions is the Fenton reaction, where iron ions (or other metal ions like copper or tungsten) catalytically decompose hydrogen peroxide, forming highly reactive hydroxyl radicals. [8]-[11] Furthermore, metal nanoparticles can penetrate cell walls or adhere to them externally, releasing ions that are toxic to the microorganisms. [12], [13] Additionally, metal particles produced by electrode erosion can lead to promising applications in nanomaterial synthesis. [14] On the negative side, metals in aqueous solutions are expected to pose toxicological and environmental challenges. [15], [16] For instance, if plasma processes are used for water purification, it is crucial to make sure that erosion does not introduce dangerous metal contaminants that are ultimately released in the environment. The plasma-induced erosion of electrodes immersed in liquid media has been widely studied over the last 20 years. [7], [8], [17]–[19] Erosion has been attributed to sputtering, melting, evaporation, oxidation and electrochemical-derived processes. [4], [11],

[17], [18], [20]–[22] We have found very few works that study the erosion of high-voltage electrodes in gas-liquid environments. [10], [16] Particularly, the erosion of the gas-side electrode has been barely studied, to the best of our knowledge. We consider that it would be of interest to the plasma–liquid community to be aware of erosion of the gas-side electrode, and how it can introduce metal particles and/or ions into PAW.

In this work, we use a nanosecond-pulsed corona to produce discharges above a liquid surface. We report on the erosion of three pin electrode materials (hafnium, copper, stainless steel) and in two gas atmospheres (oxygen, air). In order to study whether electrode erosion affects the removal of contaminants, we used the dye methylene blue as model organic pollutant.

2. Experimental section

Figure 1 shows the experimental setup. The plasmaliquid reactor consists of a borosilicate glass vessel (JRV Scientific Glass Montreal, inner diameter 19.4 mm, height 83.5 mm), sealed with two home-made polytetrafluorethylene (PTFE) lids. The cathode pin is made up of a fine metal wire (Goodfellow, 0.25 mm diameter) of either hafnium (97 % purity), stainless steel (302 grade) or copper (99.99 % purity), placed about 2 mm above the liquid. The anode consists of 316L stainless steel sparger (Cole Parmer) mounted at the bottom of the reactor. Through the sparger, either compressed air or oxygen (Praxair, 99.993 % purity) was bubbled into the reactor at a flow rate of 6 mL/min. Gas was bubbled for 3 min before starting any discharge, to make sure that the gas atmosphere in the reactor was either air or pure oxygen. The reactor remained at atmospheric pressure. A cooling jacket connected to a water bath (Marshall Scientific, Thermo Neslab RTE 10 Circulating Chiller) ensured that the temperature of the liquid in the reactor stayed constant at 20.5 °C.

The electrodes were powered with a homemade diode opening switch generator, which produced a positive and a negative pulse simultaneously. The negative pulse powered the wire, and the positive pulse powered the sparger. The voltage and current waveforms were recorded simultaneously using a Tektronix TDS2024 oscilloscope, Tektronix P6015A high-voltage probes, and a Pearson 6585 current probe. We did not observe any influence of the type of gas atmosphere on the waveforms. Figure 2 shows characteristic voltage and current waveforms measured in an oxygen atmosphere.



Fig. 1. Experimental setup.



Fig. 2. Total voltage drop and current waveforms of a pulsed corona discharge in oxygen and over water.

Each liquid sample (8 mL) was treated with pulses of about 11 kV_{peak}, a Full Width at Half Maximum (FWHM) of 40 ns and a pulse frequency of 3 kHz. Reverse-osmosis water (RO, conductivity 1.2 M Ω ·cm) was used in all experiments. For the methylene blue (MB) samples, the liquid was a solution of 9 mg/L methylene blue (Fisher Scientific, M291) in RO water. At least 3 repeats were performed for each reported data point. The arithmetic mean and standard deviation of the samples were calculated.

The metal content of PAW samples was measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Thermo Scientific, iCAP 6000 Series). Before the ICP-OES measurements, the samples were digested with acid at 95 °C for 2 hours. The acids were either 4 vol% of HNO₃ for samples prepared with copper or stainless steel electrodes, or 5 vol% aqua regia (HNO₃:HCl, 1:3) for the samples prepared with a hafnium electrode. Both acids were purchased from Fisher Scientific in trace metal grade.

The concentration of MB samples was measured by UVvis absorption (Ocean Optics, USB2000 portable spectrometer) before and immediately after plasma treatment. For each measuring point, a new sample was prepared. This means that after one continuous plasma treatment (5, 10, 15, 20 or 30 min), the samples were measured by UV-vis absorption and not treated further. In order to convert the measured absorption into MB concentration, we prepared a calibration curve that related the absorption maxima of MB at 665 nm (± 0.5 nm) to different concentrations of MB. The absorption was measured in the 390-800 nm range, in BrandTech BRAND macro disposable UV cuvettes (Fisher Scientific).

3. Results and discussion

Electrode erosion

The results of ICP-OES measurements indicate that all three metal electrodes eroded and released metal into the liquid volume. Figures 3 and 4 show the results of PAW that had been treated with an oxygen or air plasma, respectively.



Fig. 3. Metal concentration in PAW measured by ICP-OES. These results were obtained with corona discharges in oxygen, for different electrode materials (hafnium, copper, stainless steel). Note that iron represents the metal release from the stainless steel pin electrode.

Regarding the results obtained in an oxygen atmosphere (Figure 3), hafnium is the electrode that erodes the most, followed by copper. For these two electrodes, we see that an increased corona treatment time leads to a higher deposition of metal into the PAW. After an initial erosion period of 10 min, the metal deposition trend appears linear. The results obtained with a stainless steel electrode are quantified by measuring the iron content in PAW. Although the iron quantity was above the detection limit, it was around the iron quantitation limit (about 0.012 mg/L). This can explain why the values of iron fluctuate, and do not show a clear trend with increasing corona treatment time.

In the case of corona discharges in an air atmosphere (Figure 4), copper is the electrode that erodes the most, about a factor of 7 more than in oxygen. For the hafnium electrode, the results of discharges in air are in the same range than in oxygen. Stainless steel remains the electrode that erodes the least. However, stainless steel does erode more in discharges in air than in oxygen. In the longest corona discharge time of 20 min, the concentration of iron is 4 times higher in air compared to oxygen.



Fig. 4. Metal concentration in PAW measured by ICP-OES. These results were obtained with corona discharges in air, for different electrode materials (hafnium, copper, stainless steel). Note that iron represents the metal release from the stainless steel pin electrode.

Methylene blue degradation

Methylene blue (MB) solutions were plasma-treated for different discharge times, and the discoloration of the dyed solution was tracked by UV-vis absorption. The results are shown in Figure 5. In all studied cases, discharges in oxygen led to a faster degradation of the dye than in air. In oxygen, the dyed solution was completely discolorated after 20 min, whereas in air a 30 min treatment was not enough to achieve complete discoloration. This can be attributed to the different RONS that are formed in air and oxygen. For instance, our ongoing work shows that the concentration of hydrogen peroxide in PAW produced with discharges in oxygen is significantly higher than in air (data not reported here).

We did not observe any significant effect of the choice of electrode material on the dye degradation. Especially in the case of discharges in oxygen, the degradation trend is almost identical. If we plot the natural logarithm of the MB concentration versus the treatment time, we see that the degradation follows first order kinetics (graph not shown here). The first-order rate constants are $k_{\rm Hf} = 0.2293$ min⁻¹ ($R^2 = 0.994$) for the hafnium electrode, kss = 0.2253 min⁻¹ ($R^2 = 0.980$) for the stainless steel electrode, and $k_{\rm Cu} =$ 0.2308 min⁻¹ ($R^2 = 0.967$) for the copper electrode.

4. Conclusions and outlook

We used nanosecond-pulsed pin-to-liquid corona discharges and studied the erosion of the electrodes. For all pin electrodes (hafnium, copper, stainless steel) and gas configurations (oxygen, air), we confirmed that electrode erosion leads to the release of metals into the treated liquid. We did not find any influence of the electrode material on the degradation of methylene blue.

Ongoing work studies how electrode erosion may affect long-lived RONS in the post-discharge period, and the link between the electrode erosion patterns on the surface and the produced metal products (dissolved ions or metal nanoparticles). The formation of nanoparticles could be of interest for various applications such as nanomaterial synthesis and plasma medicine.



Fig. 5. Methylene blue (MB) concentration as a function of the corona treatment time, for different electrode materials and gas atmospheres.

5. References

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