THE ELECTROCHEMICAL REACTORS SYNERGY PROVIDED BY COUPLING WITH OTHER PROCEDURES

BY

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Abstract. Cold plasma electrical discharges have been more used recently for various applications from air and compounds depollution, surface treatments for plastic or metallic surfaces, to inducing useful biologic effects.

The perspectives focused on developing industrial scale applications using cold plasma for treatments in Corona, Dielectric Barrier Discharge (DBD) or GLIDARC reactors, confirmed at small scale experimental level, support choosing the last option, due to the advantages suggested by operation in atmospheric pressure, supplied with alternative current at industrial frequency, with useful power up to 2.5 kW per module.

Increasing the electrochemical efficiency of the cold plasma treatments always remains an important concern, considering the performance of these treatments but especially the possibilities of decreasing the costs implied by these treatments.

This paper proposes and analyses the possibilities of increasing the electrochemical efficiency for cold plasma treatments, outlining directions for improving the performance of a reactor module on one side (E. Hnatiuc et al., 2002; E. Hnatiuc, 2009), but also taking advantage of the synergy obtained with complementary catalysis or photo-catalysis treatments.

Key words: Cold plasma; GLIDARC.

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1. Introduction

Cold plasma electrochemical reactors, more used for various applications, (from compound or air depollution, bacterial discontamination, treatments for metallic or plastic surfaces, up to seed treatments or ensuring biocompatibility of materials used for implants and human tissue), use Corona, DBD, GLIDARC discharges and sometimes luminiscent discharges, obtained in direct or alternative current, at industrial or high frequency (E. Hnatiuc et al., 2002; Brisset et al., 2007; Brisset et al., 2008; Gavril et al., 2009).

Parameters for these types of discharges are summarized in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Corona</th>
<th>Pulsed DBD</th>
<th>Luminiscent</th>
<th>GLIDARC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge</td>
<td>&gt;10</td>
<td>100</td>
<td>5</td>
<td>5...20</td>
</tr>
<tr>
<td>$U$, [kV]</td>
<td>$&lt;10^{-5}$</td>
<td>$&lt;10^{-3}$</td>
<td>$&lt;10^{-3}$</td>
<td>$5...20$</td>
</tr>
<tr>
<td>$I$, [A]</td>
<td>$&lt;10^{-5}$</td>
<td>$&lt;10^{-3}$</td>
<td>$&lt;10^{-3}$</td>
<td>$2,000$</td>
</tr>
<tr>
<td>$p$, [atm]</td>
<td>500</td>
<td>500</td>
<td>$&lt;500$</td>
<td>$2,000$</td>
</tr>
<tr>
<td>$T$, [K]</td>
<td>$&lt;10^{-6}$</td>
<td>$&lt;10^{-3}$</td>
<td>$&lt;10^{-4}$</td>
<td>$&lt;10^{-2}$</td>
</tr>
<tr>
<td>$\chi$</td>
<td>10$^9$</td>
<td>10$^{-5}$</td>
<td>10$^{-4}$</td>
<td>10$^{-2}$</td>
</tr>
<tr>
<td>$J$, [A/cm$^2$]</td>
<td></td>
<td></td>
<td></td>
<td>10$^{-2}$</td>
</tr>
</tbody>
</table>

GLIDARC type reactors (E. Hnatiuc, 2009), offer advantages concerning the simplicity of the device, robustness, operation in atmospheric pressure conditions, at normal environment temperature, supplied at 50 Hz industrial frequency, but also concerning the values of some parameters characterizing the useful electric discharge like specific energy, $q$, and discharge power, $P_d$, as can be observed in Table 2.

<table>
<thead>
<tr>
<th>Discharge Type</th>
<th>Corona</th>
<th>DBD</th>
<th>GLIDARC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_d$, [W]</td>
<td>10...50</td>
<td>0.5...5</td>
<td>2,500</td>
</tr>
<tr>
<td>$w_s$, [J/L]</td>
<td>10</td>
<td>20...30</td>
<td>400</td>
</tr>
</tbody>
</table>

The basic configuration of a GLIDARC type cold plasma electrochemical reactor is presented in Fig. 1, pointing out the insulating enclosure (1), that houses the divergent metallic electrodes (2).

Due to the high voltage power supply, HV, the useful electrical discharge (3) is ignited between the divergent electrodes, “gliding” along the
axial direction of the reactor, due to the flow of gas injected through the nozzle (4) but also due to electromagnetic forces.

![Diagram of a GLIDARC type reactor](image)

**Fig. 1 – Configuration of a GLIDARC type reactor.**

The operation of these devices is based on active species (electrons, positive ions, excited particles, photons), generated by the useful electrical discharge, that allow obtaining meta-stable radicals, able to maintain useful electrochemical reactions, suited for the foreseen treatment.

Evaluating the performance of these reactors and comparing various constructive configurations and types of reactors implies using quality indicators, such as, (E. Hnatiuc et al., 2002)

a) *The electrical power of the discharge, $P_d$, [W], defined as the electrical power measured directly at the electrodes, and the efficiency of the power supply*

\[
\eta = \frac{P_d}{P_1},
\]  

where $P_1$ is electrical power consumed by the power supply.

b) *The specific energy of the electrical discharge, $q$, [J/L], which permits to characterize the electrochemical reactivity of the reactors*

\[
q = \frac{P_d}{Q},
\]  

c) *The global indicator inlet–outlet, $K_1$, [J/kg], defined as the ratio between the electrical energy of the discharge, $W_d$, [J], and the mass treated into the reactor, $M$, [kg]*

\[
K_1 = \frac{W_d}{M},
\]
which allow to estimate the cost of the treatment (taking into account the electrical efficiency, $\eta$) and comparing different types of reactors.

The evolution of the GLIDARC type reactors has been continuously pursuing the increase of the electrochemical efficiency for the performed treatments, pointing out the following directions:

a) increasing the interface (contact area) between the species generated by the discharge and the treated target by designing devices with volumetric or rotary discharge;

b) increasing the power of the useful discharge and especially increasing the efficiency of the power supply, eventually using auxiliary electrodes that allow the control and adjustment of the main discharge.

This paper proposes new solutions for increasing the electrochemical efficiency of the GLIDARC type cold plasma treatments, by coupling these with catalytic or photo-catalytic treatments.

2. The GLIDARC – Catalysis Coupling

Coupling GLIDARC type reactors and catalysis pursues enabling known synergy effects, specific to these methods, which leads to the increase of the overall electrochemical efficiency of the used ensemble. For this purpose, catalytic filters can be used, placed downstream of the GLIDARC reactor, as illustrated in Fig. 2, also to benefit offered by thermal energy provided by the flow of gas, stored during the cold plasma treatment, due to the fact that the optimal temperature for catalysis, which depends on the type of material that is used, usually exceeds 400°C.

![Fig. 2 – Setup for GLIDARC – catalysis coupling.](image)

Such a catalytic filter consists of a thermo-resistant base (ceramic or metallic) containing a large number of cells which allow placing the active materials, in the form of alumina or rare metal crystals (platinum, palladium or rhodium).

The performances of plasma process can be considerably increased by adding a catalyst at the outlet of the reactor. For example the reforming of isooctane at the same energy injected and for the same gas/liquid flow rates increases up to 25 times in efficiency when added a pre-processing catalyst (Sobacchi et al., 2002) and the energy consumption and conversion rate follow
a similar improvement. In this case, the catalytic section is a stainless steel reactor placed inside a tubular furnace. The tube is packed with catalytic media. Some times, when the energy injected into plasma is important and the gas temperature is high enough to entertain the oxidation reactions, the catalyst can be placed at the outlet of the reactor (Petitpasa et al., 2007).

Observing the significant increases of the overall performances, one can say that the most of the reforming is performed thanks to the catalyst. Efficiency of the stand alone catalyst is of 40%. Thus, coupling a GLIDARC reactor to a catalyst increases the efficiency due to the fact that plasma allows to reach higher temperatures more rapidly. The application of the coupling of a plasma reactor with a catalyst uses the plasma during transient regimes, whereas the catalyst would be more likely to produce hydrogen efficiently in permanent use. In the field of catalyst addition, PSFC team has tried various systems such as honeycomb, ceramic or metallic catalyst (Bromberg et al., 2001) on different fuels (diesel, methane, ethanol, soybean oil). Again, performances of the reforming process were increased (around an extra 15% for both efficiency and conversion rate results).

The chemical reactions which take place in these catalytic filters can be reduction reactions or oxidation reactions, implying the careful choosing of the operating parameters (temperature, pressure, passing time, gas flow velocity) in order to facilitate the desired useful reactions.

A fact to be noted is the limited life time of these catalytic filters, which imposes their replacement implying the interruption of the operation for the ensemble which represents a disadvantage. Another disadvantage is the high aerodynamic resistance of the catalytic filters which implies pressure losses and the need to use additional pumps to ensure the prescribed velocity for the flow of fluid.

The fact that obtained results using catalytic materials of alumina type are comparable to ones obtained by coupling GLIDARC and rare metals stands up as an advantage, due to the fact that accepting cheaper solutions for such treatment couplings is possible.

3. The GLIDARC – Photo-Catalysis Coupling

Photo-catalysis is based on exciting a semiconductor by means of radiation with sufficient energy to ensure the forming of electron-positive gap pairs, \((e^-, h^+)\), which have strong oxidizing-reducing properties, (E. Hnatiuc, 2009). Thus, these pairs can take part in maintaining reactions for destroying organic polluting agents, for example, as signalled by Jacoby in 1996.

The most known photo-catalysis material is TiO\(_2\), which can be excited in the UV radiation range, resulting \((e^-, h^+)\) pairs, according to reaction:

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2^* + e^- + h^+. \quad (4)
\]

A large number of works studied the UV photolysis of water in view to
purify it from organic pollutants. Gettoff (1993) has compared several methods of water purification from organic pollutants, such as UV irradiation, irradiation by sunlight with catalysts (n-TiO$_2$), and ionizing irradiation. In studies concerning UV decomposition of aqueous solutions of dichloromethane and tetrachloroethylene, the decomposition quantum yields were found to be 4 and 16 units, respectively. It was found that, upon the decomposition of these molecules, chlorine atoms can be detached due to either the direct absorption of the UV radiation by these molecules or their interaction with products of the UV photolysis of water.

In principle, the electrons ($e^-$) are trapped by oxygen molecules, forming super-oxide radical-ions while the positive gaps ($h^+$) react with the electron donors (water molecules, OH$^-$ ions), absorbed on the TiO$_2$ surface.

Considering the GLIDARC type electrical discharge specific radiation spectrum (Pellerin et al., 1996) (Fig. 3), which outlines radiations in UV spectrum, it is possible to imagine a GLIDARC type reactor with electrochemical efficiency given by the active species produced by the useful electrical discharge, but also by ($e^-$, $h^+$) pairs, generated by means of photocatalysis, in the discharge environment due to the layer of TiO$_2$, formed on the inner side of the reactor’s enclosure (Fig. 1).

![Fig. 3 – The GLIDARC type electrical discharge specific radiation spectrum.](image)

We outline the fact that the ($e^-$, $h^+$) pairs which intervene in the active areas of the GLIDARC reactor and also in the areas with a density of active
species generated by the useful electric discharge is very low, thus having a
decisive contribution for increasing the electrochemical efficiency of the
ensemble.

In addition, the 7…10 years lifetime of the TiO$_2$ film is to be noted,
comparable to the lifetime of the electrochemical reactor, an obvious advantage
which sustains this solution.

4. Conclusions

The paper proposes a method to increase the electrochemical efficiency
of the GLIDARC type cold plasma treatments by means of electrochemical
reactor – catalysis coupling, electrochemical reactor – photo-catalysis coupling,
respectively.

For the GLIDARC type reactor – catalysis coupling situation, using a
catalytic filter with alumina downstream of the reactor is proposed, considering
the optimal temperature for catalysis, the passing time through the filter and the
additional aerodynamic resistance of the filter.

For the GLIDARC type reactor – photo-catalysis coupling situation,
when the two phenomena intervene simultaneously inside the reactor, covering
also the areas where the density of active species generated by the electrical
discharge is very small, the electrochemical efficiency of the treatments can be
significantly increased, without imposing replacement operations for active
elements, (except for the electrodes), at a 7 … 10 years lifetime of the TiO$_2$.

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SINERGIA REACTOARELOR CU PLASMA RECE PRIN CUPLAREA MAI MULTOR PROCEDEE DE TRATAMENT

(Rezumat)

Descărcările de tip plasmă rece au fost folosite recent pentru diverse aplicații de la depoluarea aerului și apei, tratamentul suprafețelor din plastic sau metalice, până la inducerea de efecte biologice.

Cercetările avute în vedere pentru viitor vizează dezvoltarea la scară industrială a aplicațiilor reactoarelor de tip Corona, DBD (Dielectric Barrier Discharge) sau GLIDARC, a căror eficiență a fost confirmată la scară de laborator, și care s-au impus ca o ultimă soluție datorită avantajelor pe care le oferă prin funcționarea la presiune atmosferică, frecvență industrială și obținerea de puteri de până la 2.5 kW pe modul.

Creșterea eficienței electrochimice a tratamentelor cu plasmă rece a rămas întotdeauna un obiectiv esențial, considerând performanțele acestora, și implicit scăderea costurilor aferente tratamentelor.

Lucrarea își propune să întreprindă o analiză a posibilităților de creștere a eficienței electrochimice a tratamentelor cu plasmă rece, subliniind direcțiile de îmbunătățire directă a performanțelor reactoarelor, pe de o parte, și prin utilizarea a procedeelor complementare pe de altă parte, considerând sinergia acestor metode de tratament.