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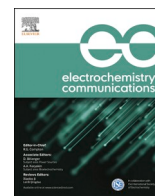
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On the impact of electrolyte temperature on contact glow discharge electrolysis

Klaus Rottach^a, Guenter Lang^b, Matteo Gastaldi^{c,d}, Claudio Gerbaldi^{c,d}, Matteo Bonomo^{d,e,*}

^a CGDE Research Lab K. Rottach, Westendorf 87679, Germany

^b Kühne Logistics University, Hamburg 20457, Germany

^c GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino 10129, Italy

^d National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Firenze 50121, Italy

^e Department of Chemistry and NIS Interdepartmental Centre, University of Turin, Via Pietro Giuria 7, Torino, 10125, Italy

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ABSTRACT

This study aims at disclosing the effect of small temperature drops (10–15 °C) of the electrolyte on Contact Glow Discharge Electrolysis (CGDE). In our experiments, we measure the temperature change of electrolyte and electrode as well as the change in current following on from the addition of, first, frozen and, second, boiling KOH aqueous solution (0.1 M). Quite surprisingly, only the addition of frozen KOH aqueous solution has a significant impact on current (+130%), caused by the decrease in electrolyte temperature (-11 °C). In contrast, the addition of boiling KOH aqueous solution has a negligible effect on current. A very similar behavior is recorded when frozen or boiling type III deionized water is used: the addition of ice has an even stronger impact on current (+145 %) and on electrolyte temperature (-14 °C), while adding boiling water has no measurable effect. Thus, we here demonstrated that electrolyte temperature is critical for managing the responsiveness of the CGDE system. Our results pave the way toward temperature controlled CGDE, a powerful tool for a greener and a more efficient environmental chemistry.

1. Introduction

The history of Contact Glow Discharge Electrolysis (CGDE) dates back to 1950 with the seminal study of Kellogg [1]. However, it took many years before CGDE has been established in literature after the rigorous experiments of Hickling and Newns, which confirmed the discharge phenomena in their study on liquid-ammonia solutions [2]. Up to date, CGDE is employed in many applications, exploiting the huge generation of heat produced and/or the production of radical species. CGDE is mainly exploited in waste-water treatment, with the plasma leading to the efficient degradation of aromatic compounds, ionic liquids, and polymers. Other applications range from synthetic chemistry to electrosurgical devices, nanoparticle fabrication and surface engineering, representing a more economical and greener alternative to the traditional technologies [3–5]. Besides these, CGDE can be also exploited as a feasible method to produce steam in continuous mode, with an efficiency of the entire process of about 80% [6]. CGDE takes place when the voltage is increased beyond a certain threshold after which the conventional electrolysis breaks down. The sudden decrease in current,

the increase in voltage through the electrodes and the generation of light around one or both the electrodes are effects all related to CGDE, a phenomenon in which the term ‘contact’ was introduced to point out that both the electrodes are soaked in liquid electrolytes [7].

Pioneering articles on the topic were mainly focused on studying chemical and physical features of CGDE, finding that the main governing factor is the Joule effect, leading to the overheating of the solvent and causing its local vaporization [8]. Once a specific value of voltage (depending on the electrolyte) commonly called breakdown voltage (V_B) is reached, a non-conventional electrolysis takes place. By increasing the voltage beyond the midpoint value (V_D), instead, a light-emitting plasma surrounding a tiny area between the electrode (cathode or anode) and the electrolyte can be generated. This process usually leads to non-faradaic chemical reactions, and it can be obtained using both aqueous and organic liquid electrolytes as well as employing molten salts [3,9]. The V_B value can be determined as the maximum of I-V curves of the CGDE, while V_D , even less evident, can be determined at the value at which a rapid increase in current takes place. Literature reports evidenced that V_D mainly depends on the polarity of the

* Corresponding author.

E-mail address: matteo.bonomo@unito.it (M. Bonomo).

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electrode and on the overall conductivity of the electrolyte [7,10], with the nature of the specific ions playing only a minor role [11]: as a rule of thumb, the higher the electrolyte conductivity the lower the V_D . Jin et al. [7] proved that V_D shows a decrease following on from the increase in ionic conductivity but, once $\sigma > 5.0 \text{ mS cm}^{-1}$, V_D is no longer affected by the nature of the anion of the Na-based electrolytes, except for the possible occurrence of side reactions (e.g., formation of Cl-based radicals, in case of NaCl electrolyte). Following on from these pioneering papers, more thorough studies were performed to clarify the role of additional variables that can influence the process. In this respect, Sengupta et al. [12] found that the electrolyte surface tension as well as its temperature are able to dramatically change the boundary conditions for the transition from conventional electrolysis to CGDE. Indeed, the electrolyte surface tension affects the growth of vapor film, and its lowering leads to decreased V_B values. On the other hand, by increasing the temperature, a lower amount of power is required to allow the local vaporization of the water (by the Joule effect), leading to a more energetically favored breakdown of conventional electrolysis. It is worth noticing that a higher electrolyte temperature seems to have a positive effect in reducing the value of both V_B and V_D , although the latter at a considerably slower rate [3]. An in-depth study about the effect of the temperature on the current and nature of anodic CGDE was also carried out by Kusmanov et al. [13].

This literature overview points out that (i) the CGDE is primarily influenced by the nature of the plasma surrounding the electrode without any influences coming from the electrolyte solution around the plasma, and (ii) no breakdown of normal electrolysis occurs at temperature below 15°C , even at high applied currents. A more comprehensive investigation was conducted by Sen Gupta who demonstrated that higher electrolyte temperatures are beneficial to the production of CGDE, as well as a higher concentration of the electrolyte and a smaller dimension of the electrode. The modification of one or more of these variables leads to an acceleration/deceleration of the charge/discharge at the interface between the active electrode and the plasma layer constituted by water vapor [3,14]. Only one-factor-a-time approaches have been proposed so far, i.e., the effect of the change in temperature and in the conductivity was analyzed separately one from each other. In the present paper, we investigate the role of the electrolyte conductivity and the temperature in modifying the CGDE phenomenon monitoring the plasma-generated current. Albeit all literature studies reported so far on CGDE describe a positive dependence on temperature, hereafter we demonstrate that this is not always true. This is an important finding, which we detail in this work, because it allows to tune the intensity of CGDE-induced plasma (measured as the supplied current), viz. the reactivity of the system under study, depending on the temperature.

2. Experimental

Potassium hydroxide (KOH, CAS 1310-58-3, purity $> 99.5\%$) was purchased from WHC GmbH and type III deionized water ($\sigma < 1 \mu\text{S cm}^{-1}$) was used during the preparation of all the solutions. The experiment was performed in a 300 ml glass jar. The jar was filled with a 250 ml aqueous KOH solution (0.1 M). The anode consisted of a stainless steel tube (diameter = 4 mm, length = 60 mm, surface area immersed in the electrolyte = 754 mm^2). The stainless steel cathode was custom-made from a sheath thermocouple (K-Type from OWON® Group): in addition to the wires for the temperature measurement, a third wire was attached to the stainless steel mantle. The third wire was connected to the cathode of the DC power source (Lincoiah CL-S-5000, 0–600 V 5000 W) during the experiment. The electrode was almost completely covered with a corundum tube for heat resistant insulation. The exposed part of the thermocouple, working as the actual cathode, had a diameter of 2 mm and a length of 15 mm (surface area immersed in the electrolyte = 97 mm^2 , area ratio cathode:anode 1:7.8). As far as we are aware, this experimental set-up has not previously been reported in the literature. The latter allows us to measure both the current evolved at the cathode

and its temperature. Some control experiments were made (not shown) to check the effect of the built-in electric field on the temperature measurements; no meaningful effect was detected and thus the temperature measurement is reliable. Furthermore, a standard K-type sheath thermocouple (OWON®) was placed within the jar to determine the electrolyte temperature. All these components were attached or led through the top cover, which was screwed onto a glass jar. CGDE figures of merit (voltage and current) and other key parameters such as the temperature of the cathode and of the electrolyte were recorded and digitally stored onto OWON® 18-B Multimeters (sampling rate 2 points per second). Each experimental step was started when steady-state conditions were reached. Fig. 1 shows the chart flow of the reported experiments. After each reaction step, an aliquot of the solution was collected to measure the ionic conductivity. For both the main solution and the successive additions, i.e., frozen KOH aqueous solution (KOH_f) and boiling KOH aqueous solution (KOH_b), the same batch of KOH aqueous solution was used. The KOH_f was stored in a freezer at -20°C and it was taken out immediately before the experiment. Solution conductivity was measured by a conductometer Cond 730 purchased by WTW inoLab.

3. Results and discussion

As soon as the experiment is started, the voltage is raised very slowly (1 V s^{-1}) to clearly detect both the V_B and V_D values. A summary of the data recorded in all experiments is reported in Table 1. After 90 s, V_B is reached with a recorded voltage of 87 V and an associated current of 2.8 A; then, as expected after V_B , a further increase in applied voltage leads to the current decrease until the V_D (131 V) is reached, with the latter associated to a minimum point in the current trace (0.52 A). Throughout this timeframe, the electrolyte temperature slightly monotonically increases up to 85°C (at V_B) and up to 92°C when V_D is reached. On the other hand, the cathode temperature rises faster up to 97°C at V_B and then it remains constant ($\pm 1^\circ\text{C}$). After V_D , no matter the increase in the applied voltage (V_{app}), the current stabilizes at a constant value ($0.66 \pm 0.04 \text{ A}$) until a $V_{\text{app}} = 192 \text{ V}$ is reached. At this stage, plasma is starting to be formed as proven (i) by a sudden current raise (1.01 A, +52%, then stabilized at 0.94 A, +42%) and, more importantly, (ii) by an extremely fast increase of the cathode temperature that jumps from 97 to 1130°C within 10 s. When CGDE occurs, the temperature increase is limited to the electrolyte volume close to the active electrode [12] (i.e., the cathode in our case), whereas the temperature of the bulk electrolyte does not show any change (97°C). Once the CGDE is activated, the potential is kept constant at $190 \pm 1 \text{ V}$.

As commonly reported in CGDE experiments, after the sudden current increase following the plasma creation, the current tends to slowly decrease until a steady state is reached. At this stage, the current is higher than the one before the plasma trigger (0.7 vs 0.6 A) and it remains constant (as well as the other monitored parameters). After 5 min, two pieces of KOH_f (0.1 M, total volume of 10 ml) are dropped into the reaction jar. Due to the relatively high electrolyte temperature (i.e., boiling water), the two pieces melt almost immediately, inducing a slight but meaningful reduction of the whole electrolyte temperature (down to 86°C). Following on from melting, a dramatic increase in both electrode temperature and current is recorded (Fig. 2): the latter increases up to 1.6 A (+130%) whereas the former exceeds 1300°C (upper limit of our instrumentation). As depicted in Fig. 3, after the addition of KOH_f , the CGDE becomes more intense (i.e., louder and brighter) as also witnessed by the increase in the measured current. Aiming at a more quantitative analyses, we also employed a luxmeter (place at 30 cm away from the experimental set-up) to monitor the change in brightness following on from the addition of KOH_f (Fig. 3, bottom frame). Before the experiment, an illuminance (due to the environment) of 20 lx was measured which starts to increase as soon as the voltage is increased reaching a peak of 250 lx at V_B ; then, the illuminance starts to gradually decrease (e.g. 150 lx at V_D) reaching a

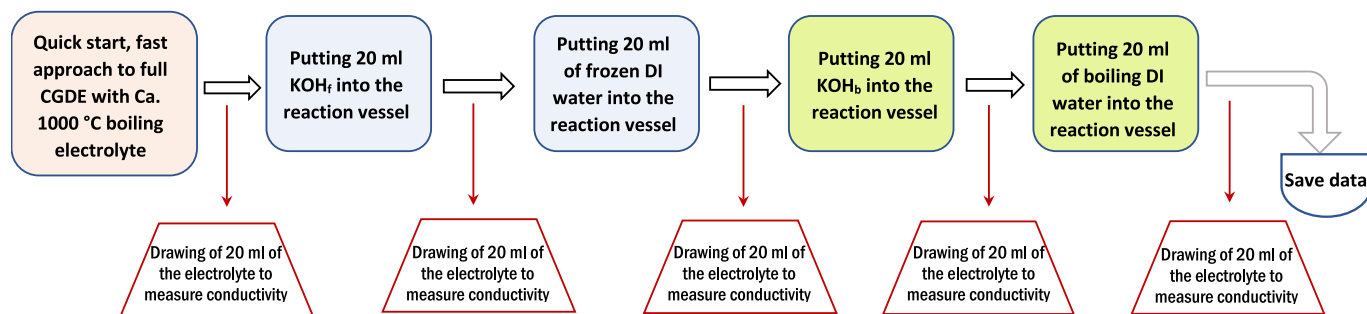


Fig. 1. Chart flow of the experiment timeline.

Table 1

Key parameters monitored throughout the experiment.

	Voltage / V	Current / A	T _{Electr} / °C	T _{cath} / °C	σ / (mS*cm ⁻¹)
Start	0	0.00	82	83	
V _B	87	2.81	85	97	
V _D	131	0.52	92	97	
Steady-state ^a	184	0.69	96	98	20.1
CGDE peak	192	1.01	96	426	
Steady-state ^a	191	0.77	97	1147	20.1
KOH_f addition					
Peak	191	1.58	86	1300	
Steady-state ^a	191	0.70	97	1085	20.4
Frozen DI H₂O addition					
Peak	190	1.71	83	1264	
Steady-state ^a	191	0.70	97	1086	18.1
KOH_b addition					
Peak	190	0.85	97	1163	
Steady-state ^a	191	0.70	97	1086	19.7
Boiling DI H₂O addition					
Peak	191	0.73	97	1107	
Steady-state ^a	191	0.68	96	1080	19.1

^a Reached when the value of all the parameters is constant.

plateau of 100 lx during CGDE. As soon as KOH_f is added to the solution, the illuminance rises again (maximum at 260 lx, corresponding to the minimum of electrolyte temperature). Then, in the following 150 s, all the modified parameters returned to their pre-addition values. Quite remarkably, notwithstanding the addition of KOH_f (a source of K⁺ and OH⁻ ions), the overall conductivity of the solutions only slightly increased (20.4 vs 20.1 mS cm⁻¹, measured before the manipulation); such evidence is somewhat counterintuitive considering the intensification of plasma recorded. As reported in the literature [11], a slightly higher electrolyte conductivity (+1.5%) should not be enough to generate a dramatic modification in CGDE.

To further shed light on this somehow unexpected behavior and to clarify the role of the decrease in the electrolyte temperature on plasma generation, we planned an additional experiment: once the electrochemical parameters reached again the steady state, we added 10 ml (same volume as the first addition) of frozen Type III deionized water (*i.e.*, without KOH). Once more, a remarkable decrease of the electrolyte temperature (down to 83 °C) is coupled to an intensification of plasma production proven by both a jump in current (1.66 A, +145%) and a rising in the electrode temperature (+180 °C) (Fig. 2). One should note that the higher the temperature drop, the higher the current increase. In the control experiment also the illuminance shows a remarkable increment (*i.e.* from 75 to 180 lx, right before and after the addition of ice, respectively, Fig. 3, bottom frame). As far as we are aware, this is the first report of such a remarkable electrolyte temperature-induced effect in CGDE. As expected, after the addition of deionized water, the overall

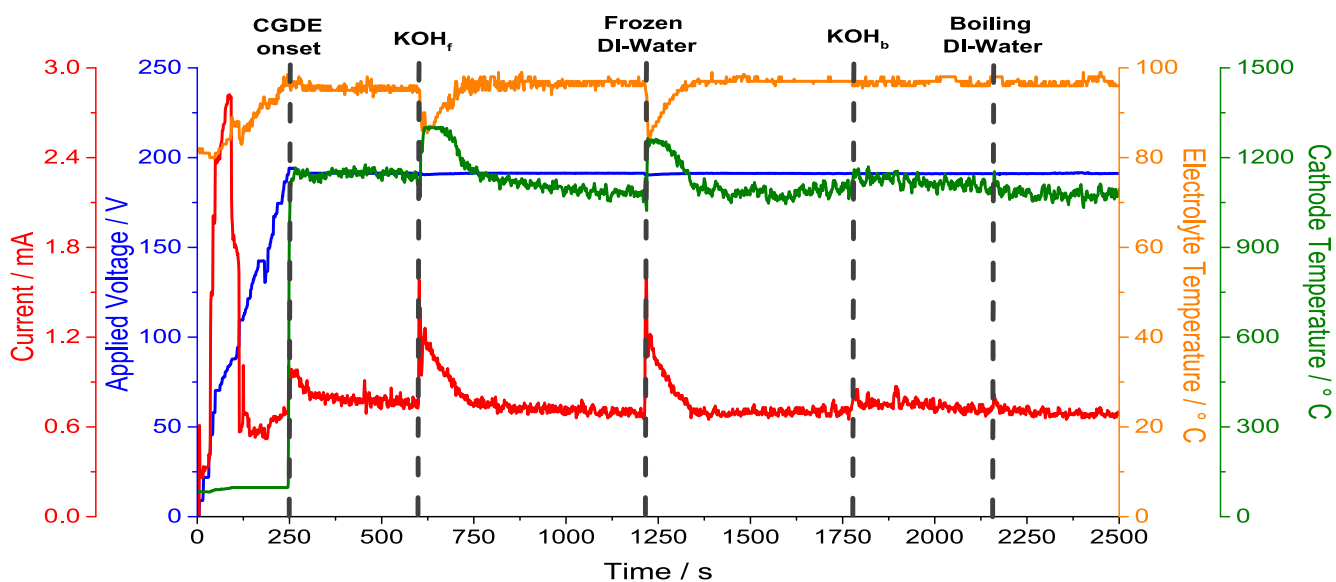


Fig. 2. Data traces of the monitored parameters: current (red), applied voltage (blue), electrolyte temperature (orange) and cathode temperature (green) for the whole experiment. Vertical dotted grey lines evidence the time of the CGDE trigger and of the additions of the different solutions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

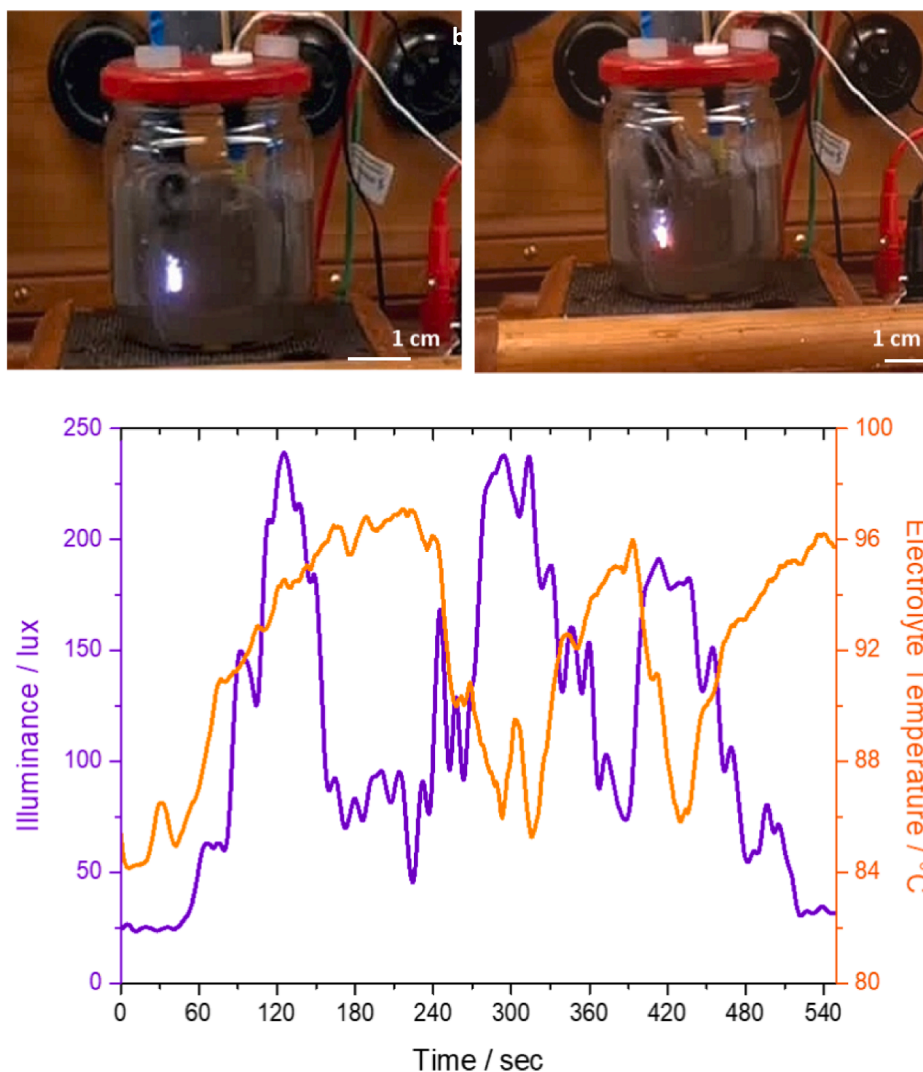


Fig. 3. Snapshots extracted as frames from the video recorded during the experiment right before (top left) and after (top right) the addition of KOH_b . Evolution of the illuminance of the cathode and the electrolyte temperature (bottom). The experiment is conducted in the same condition of the one reported in Fig. 2, but in a different timeframe.

conductivity of the solution decreases to 18.1 mS cm^{-1} , this proving a clear decoupling of the reported effect from solution conductivity.

To support our findings, we conducted two additional experiments in which the same amount (10 ml) of KOH solution and Type III deionized water was added; yet, in this case, the solution was added at boiling temperature (97°C) and not as frozen. This should avoid any decrement in the electrolyte temperature and will give us the chance to confirm our findings. Noteworthy, after the addition of both boiling solutions, a negligible increase in current and electrode temperature values is detected (+20% and +7%, when KOH_b or boiling water is added, respectively) not leading to any significant modification of the plasma intensity. After the addition of KOH_b , the solution conductivity increases up to 19.7 mS cm^{-1} (all data are shown in Fig. 2 and tabulated in Table 1). The increase in conductivity could be seen as a further proof of the insensitivity of the plasma to the addition of boiling solutions: indeed, no additional ions are consumed within the plasma triggering and thus all the added ones could contribute to the electrolyte conductivity. In fact, after the addition of boiling deionized water, the only detectable effect is a slight reduction in the overall conductivity of the solution (19.4 mS cm^{-1}), resembling the dilution effect.

4. Conclusions

This paper analyses the impact of the electrolyte temperature on the CGDE process. In our experiments, frozen solutions are added to the electrolyte to induce a temperature drop of some degree Celsius. For the first time, we evidenced a strong negative association between electrolyte temperature, the intensity of the plasma (i.e. a higher brilliance as measured by the illuminance, +200%), and the level of current (+130%). The use of KOH or Type III deionized water frozen solutions led to similar behavior proving that the main reason for plasma intensification is ascribable to the decrease in the electrolyte temperature rather than a modification in the electrolyte conductivity, with the latter playing only a marginal role. To further support our findings, we successively added KOH_b and boiling solution of Type III deionized water: as a result, only a limited increase in powered current could be detected. Albeit further investigation is required to better clarify the evidenced temperature-dependent behavior, our findings could pave the way toward further optimization of CGDE application at sub-boiling temperature.

CRedit authorship contribution statement

Klaus Rottach: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Project administration, Funding acquisition. **Guenter Lang:** Methodology, Validation, Formal analysis, Writing – review & editing. **Matteo Gastaldi:** Validation, Formal analysis, Writing – original draft. **Claudio Gerbaldi:** Resources, Data curation, Writing – review & editing, Funding acquisition. **Matteo Bonomo:** Conceptualization, Methodology, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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