

Facile thermal activation of low-grade fuel coke for electro-reduction of hydrogen peroxide from air and water

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Hydrogen peroxide (H₂O₂) is a green oxidant widely used in the paper and textile industries and advanced oxidation of wastewater. It is also considered a potential energy carrier in fuel cells. The annual global production of H₂O₂ is around 6 million tons, with a growing rate of 3% in the next 5 years (Li *et al.* 2022). Currently, H₂O₂ production is dominated by the anthraquinone process, an energy-intensive, hazardous, and toxic process involving chemical modifications with organic solvents. Hence, an environmentally friendly, non-hazardous, and cost-effective alternative to the anthraquinone process is required to provide a sustainable supply of H₂O₂.

The electrosynthesis of H₂O₂ *via* the 2-electron oxygen reduction reaction (ORR) is a clean and cost-effective process, considered one of the most promising alternatives to the anthraquinone process. As such, intensive research in developing efficient catalysts to promote the 2-electron ORR is taking place (Huang *et al.* 2023). Among these catalysts, carbon-based electrocatalysts from waste sources stand out to promote a circular economy. Low-grade petroleum coke, known as fuel coke (FC) is a growing waste from the gas and oil industry, generally used as fuel due to its low quality to be used for electrodes in the metal industry. FC is toxic, containing heavy metals and sulfur, which leads to air and water contamination. Hence, an alternative use for FC is needed to improve the sustainability of the gas and oil industry and prevent environmental contamination.

In this context, we propose a facile thermal activation of FC as granular catalyst for the electro-reduction of hydrogen peroxide from air and water in a fixed bed reactor. The FC granules are directly activated without need for ball milling or use of solvents and binders, which improves the cost and sustainability of the process, as opposed to most materials developed (Huang *et al.*, 2023). The operational factors are evaluated and optimized using a design of experiments (DoE). To our knowledge, this is the first time that low-grade fuel coke is used as electrocatalyst for hydrogen peroxide production without modification with solvents or binders and the operational conditions optimized following a DoE systematic approach.

Materials and methods

Green coke fuel grade was obtained from Repsol (Mostoles, Spain). Sodium sulfate, hydrochloric acid, and potassium titanium oxide oxalate dihydrate were purchased to Sigma-Aldrich. All aqueous solutions were prepared with Milli-Q water (18.2 MΩ cm).

Prior to calcination, granular green coke (GC) of diameter 2-4 mm was soaked in 0.1 M HCl for 30 min to remove impurities and grease on its surface, rinsed thoroughly with DI water and dried at 80°C overnight.

A sample of 17 g of GC was calcined in under nitrogen atmosphere with a flow rate of 100 ml/min to the target temperatures of 600°C, 700°C and 800°C, leading to calcined materials GC-600, GC-700 and GC-800 respectively. The heating ramp was 4 C/min to 420°C for 30 min followed by a second ramp of 4 C/min to the target temperature for 80 min. Samples were rinsed with DI water and dried at 80°C again prior to use. Samples were weighted before and after calcination to determine the yield. Elemental analysis (C, N, S, H, O) and BET analysis were performed before and after calcination.

The calcined granules were tested for hydrogen peroxide production in an up-flow cell of 15 cm high, bed volume of 10 ml, and total cell volume of 40 ml. Air was sparged at the bottom at a flow rate of 1 l/min. The electrolyte was 0,05 M Na₂SO₄ with an inlet at the bottom and outlet at the top. The flow was controlled with an HPLC pump. The anode was a Pt wire located at 1 cm of the cathode top. The cathode current collector was a piece of graphite rod (1 cm long; 1 cm diameter). The current collector was completely immersed in the granular material and connected to a Ti wire to connect the power supply, which was used to fix the current. The Ti wire was isolated from the electrolyte to avoid hydrogen evolution. The cathode potential was measured with an Ag/AgCl (3M) reference electrode, which was immersed in the catalyst bed. The electrochemical cell run in continuous mode and electrolyte at the outlet stabilized immediately after collection with potassium titanium oxide oxalate and measured spectroscopically at an absorbance of 405 nm.

The effect of flow rate, current input and calcination temperature on H₂O₂ concentration, H₂O₂ production rate and faradaic efficiency (Huang *et al.*, 2023) was assessed using a 3-factorial DoE. The experiments lasted for 30 min, when the responses reached a steady state value.

Results and discussion

Elemental analysis of raw and calcined GC revealed a high content in carbon (>97%) and sulfur content around 7%. The BET analysis indicates a surface of around 2 m²/g, which suggests that the electrochemical processes are superficial. The yield after calcination is over 85% in all cases. The responses selected to evaluate the process are H₂O₂ concentration (mg/l), H₂O₂ production rate (g/lh) and faradaic efficiency (%). Figure 1 shows the Pareto plots for the responses, respectively. The most influential factors depend on the selected response and are not the same for all responses. In the case of H₂O₂ concentration (Fig. 1, left), the calcination temperature is the most significant factor, with a positive effect of 12 mg/l increase per 100°C of calcination temperature. Increasing the calcination temperature from 600 to 800°C promotes the graphitization of the material increasing its

conductivity, as well as oxygen-rich functional groups, which promote the 2-electron ORR (Han et al., 2020).

Conversely, the H_2O_2 production rate is positively affected by flow rate with an increase of 150 g/lh per 5 ml/min increase (Fig 1., middle). In this case, the interaction between flow rate and temperature becomes significant, followed by the main effect of temperature. This is probably due to higher probability of H_2O_2 degradation at low flow rates due to increased contact time. The faradaic efficiency is influenced significantly by all factors and the second order interferences, with a positive effect of the calcination temperature and flow rate, and negative of current applied (Fig. 1, right). This again is because the material is probably more efficient in performing the 2- e ORR at higher calcination temperatures, and because at higher currents, side reactions, like hydrogen evolution and H_2O_2 decomposition are favored. This is corroborated by the cathode potentials, which are 0.7 V at 10 mA, and 1.2 V vs. Ag/AgCl at 30 mA (pH=7). These results illustrate the importance of assessing the operational factors simultaneously to account for interferences.

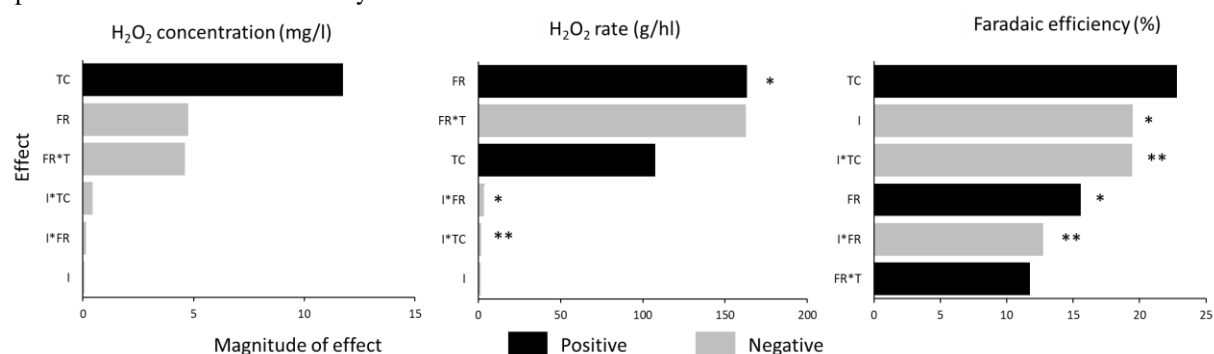


Figure 1. Pareto Plots of the linear models fitted with the design of experiments for the factors I: Current applied (mA); FR: Flow rate (ml/min); Tc: Calcination temperature ($^{\circ}\text{C}$). Significance values: $p < 0.1$:*; $p < 0.01$:**.

Considering only the H_2O_2 production, the response surface shows a maximum production of 37 mg/l (Fig. 2, left) and 550 g/lh (Fig. 2, right) at high calcination temperatures and low flow rates, comparable to the control with graphite felt. However, the factors do not interact in the same manner, with a quadratic effect in the latter.

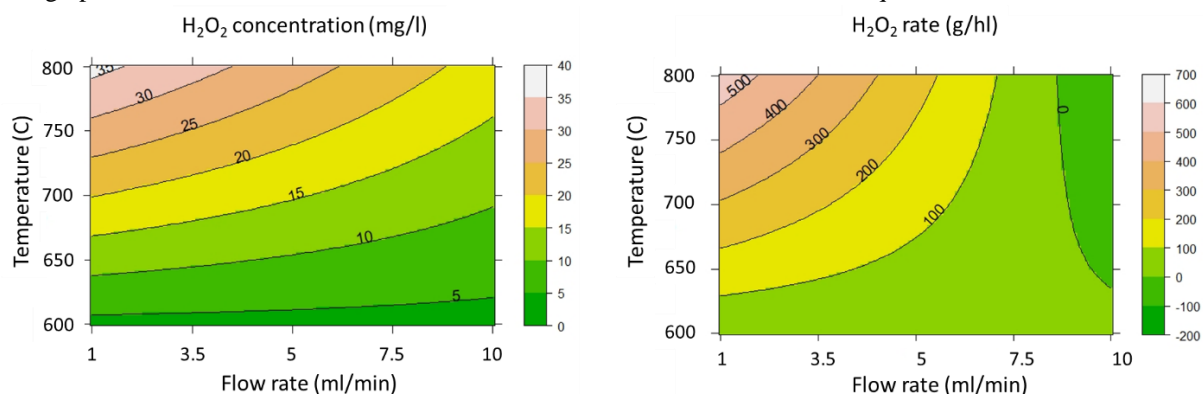


Figure 2. Response surfaces for hydrogen peroxide concentration (mg/l, left) and hydrogen peroxide production rate (g/lh, right) considering the calcination temperature ($^{\circ}\text{C}$) and flow rate (ml/min) as factors. p values < 0.01 .

Conclusions

This work proves a facile thermal activation of low-grade granular fuel coke for electrocatalytic H_2O_2 production in an up-flow fixed bed reactor. The simultaneous assessment of current, flow rate and calcination temperature show that calcination temperature is the most influential factor to maximize the concentration of H_2O_2 , with a maximum of 37 mg/l at 30 mA, 1 ml/min and 800°C similar to commercial graphite felt, whereas the maximum faradaic efficiency of 95% is reached at 10 mA, 5 ml/min and 800°C . This work illustrates the need for simultaneous assessment of operational factors on the electro-synthesis of H_2O_2 and the need for a multi-objective approach of faradaic efficiency and H_2O_2 production for an efficient operation.

Acknowledgement

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