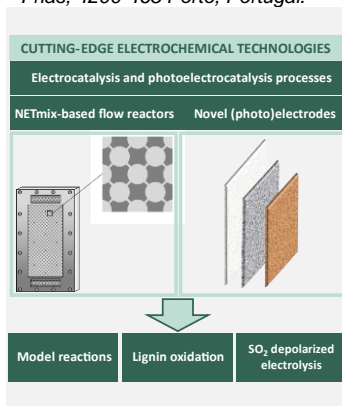


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Pioneering electrochemical technologies for producing value-added chemicals and fuels have been developed by the Environmental Engineering Group at the LSRE-LCM/ALiCE. These novel technologies include: 1) the well-established electrocatalysis (EC) process and the emerging photoelectrocatalysis (PEC) process, 2) disruptive flow reactors with enhanced mass transfer based on the NETmix static mixer, and 3) novel (photo)electrodes. They have been applied to the production of 1) *p*-anisaldehyde (PAA) from 4-methoxybenzyl alcohol (4-MBA) as a model synthesis reaction, 2) phenolic compounds derived from lignin found in black liquor, a waste stream from paper and pulp processing, and 3) hydrogen and sulfuric acid through sulfur dioxide depolarized electrolysis (SDE), using sulfur dioxide, an industrial emission gas, and water. The latter two applications bring the concept of circular and self-sufficient economy into practice.

### Introduction

Electrocatalysis (EC) and photoelectrocatalysis (PEC) are innovative and environmentally friendly processes that have gained attention in the field of synthesis of chemicals and fuels. Significant implementation barriers of these processes regard mass transfer limitations in the existing reactors and the lack of stable (photo)electrodes to foster high productivity in specific synthesis reactions. Mass transfer limitations can be overcome by developing novel flow reactors of meso/micro dimensions [1]. Advancements in the development of suitable (photo)electrodes primarily involve the use of adequate (photo)catalyst materials and deposition methods.

This work addresses the development of advanced (photo)electrochemical technologies for the production of chemicals and fuels. These technologies integrate EC and PEC processes with novel (photo)electrochemical flow reactors based on the NETmix static mixer, known as *e*-NETmix reactors, and innovative (photo)electrodes. The following applications are envisaged: 1) conversion of a primary alcohol, 4-methoxybenzyl alcohol (4-MBA), into its aldehyde, *p*-anisaldehyde (PAA), as a model synthesis reaction, 2) conversion of lignin in black liquor, a waste stream from paper and pulp processing, into phenolic compounds, and 3) conversion of sulfur dioxide (SO<sub>2</sub>), an industrial emission gas, and water (H<sub>2</sub>O) into hydrogen (H<sub>2</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) through the SO<sub>2</sub> depolarized electrolysis (SDE).

### Material and Methods

*e*-NETmix reactors, illustrated in Figure 1, correspond to filter-press (photo)electrochemical reactors where the NETmix static mixer acts as a

fluid distributor. The NETmix static mixer consists of a network of unit cells formed by cylindrical chambers interconnected by prismatic channels arranged at a 45° angle with the chamber axis [2]. A provisional patent application on *e*-NETmix reactors, encompassing distinct reactor configurations, was recently filled out [3]. *e*-NETmix reactors were characterized by the global mass transfer at different Reynolds numbers (*Re*) using the limiting current technique for the ferricyanide-ferrocyanide reversible reaction and compared with various commercial and lab-assembled reactors.

Various electrodes and photoelectrodes have been fabricated, with particular emphasis on photoanodes with niobium-doped titanium dioxide (TiO<sub>2</sub>:Nb), produced via d.c. pulse reactive magnetron sputtering, and hematite (α-Fe<sub>2</sub>O<sub>3</sub>), produced via ultrasonic-spray deposition. These materials are highlighted for their exceptional stability and photoactivity.

### Results and Discussion

*e*-NETmix reactors achieved volumetric mass transfer coefficients (*k<sub>m</sub>A*) up to  $\sim 5.1 \times 10^{-1} \text{ s}^{-1}$  and mass transfer coefficients (*k<sub>m</sub>*) up to  $\sim 2.7 \times 10^{-4} \text{ m s}^{-1}$  for a *Re* of 1750. The *k<sub>m</sub>A* and *k<sub>m</sub>* values in these reactors are up to  $\sim 54$ -fold and  $\sim 24$ -fold higher, respectively, compared to those given in various lab-assembled and commercial electrochemical flow reactors mentioned in the literature. The superior mass transfer in *e*-NETmix can be mainly attributed to using a fluid distributor with a NETmix network able to force convection and promote the development of a laminar chaotic flow regime.

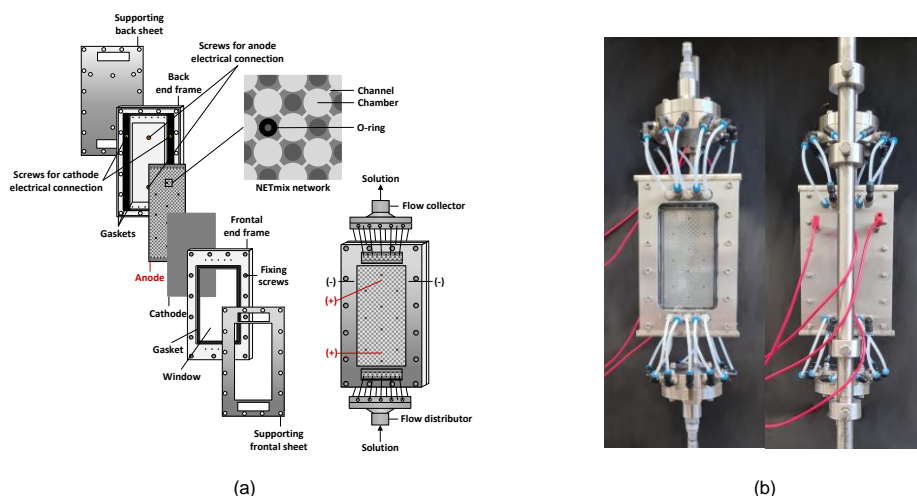
The application of a *e*-NETmix reactor to the generation of PAA from the selective oxidation of 4-MBA using the EC process with a bare fluorine-

doped tin oxide (FTO) anode proved to facilitate the use of more appealing operating conditions without loss of productivity compared to a conventional electrochemical reactor (Micro Flow Cell from ElectroCell, Denmark). These conditions include (i) lower  $Re$  (up to  $\sim 10$ -fold), (ii) lower concentrations of supporting electrolyte (up to  $\sim 30$ -fold), (iii) lower concentrations of initial substrate (up to  $\sim 1.5$ -fold), and (iv) a wider range of current densities (up to  $\sim 2$ -fold).

Pulp and paper industries generate high quantities of black liquor, which is the main industrial source of lignin. Black liquor is commonly burned to generate electricity and heat. To change this scenario, it is urgent to provide efficient and environmentally sound technological solutions for lignin recovery from black liquor. The lignin as high potential to produce low-molecular-weight phenolic compounds with added-value. However, the lignin selective

oxidation has presented challenges, yielding low amounts of low-molecular-weight phenolic compounds. A maximum yield of  $26 \pm 1 \text{ mg kg}^{-1}$  was achieved for the PEC process using a  $\text{TiO}_2\text{:Nb}$  photoanode at a cell potential of 0.8 V.

Water electrolysis is the primary method for producing green  $\text{H}_2$ , however it requires significant energy input. SDE presents a cost-effective alternative, with an energy requirement approximately eight times lower than that of water electrolysis. In SDE,  $\text{SO}_2$  and water are converted into  $\text{H}_2$  and  $\text{H}_2\text{SO}_4$ , utilizing an industrial emission gas ( $\text{SO}_2$ ). The produced  $\text{H}_2\text{SO}_4$  holds commercial value and can alternatively be thermochemically regenerated back into  $\text{SO}_2$ , thereby completing the Westinghouse Cycle. The study of SDE is currently in an initial phase, with focus on the design, dimensioning, and construction of an electrolyzer that incorporates the NETmix static mixer.



**Figure 1.** (a) Sketches and (b) photos of a possible configuration of a  $e$ -NETmix reactor.

## Conclusions

The synthesis of chemicals and fuels using EC and PEC processes can be enhanced by employing NETmix-based (photo)electrochemical flow reactors and innovative (photo)anodes.

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