Bilirubin Oxidase-based Cathode for Microbial Fuel Cell (MFC) Applications: The Effects of Bacterial/Pollutants' Presence on Enzyme Stability

by Carlo Santoro

Microbial fuel cells (MFCs) are promising bioelectrochemical systems with the potential for treating organic compounds and simultaneously generating electricity.[1] MFCs have been intensively studied in the last decades, but performances remain still low. One of the reasons is that the cathodes are directly exposed to the aqueous solution containing bacteria and various chemical compounds, which leads to cathode flooding and poisoning, and finally lowers the current output. In contrast, enzymes (*e.g.*, laccase and bilirubin oxidase[2]) are capable of catalyzing oxygen reduction reaction (ORR), and have been used as cathodic catalysts showing high open circuit potential (OCP), very low overpotentials, and high activity, especially in the range where MFCs work[3]. However, the main problem with enzymatic cathodes is long-term stability. In this report, we extensively characterize the trends of OCP, current density achieved at 0.25V and the polarization behavior of bilirubin oxidase (BOx) based cathode over a period of 12 days.

A single chamber (volume 130 ml) was used as the half electrochemical cell[4] (Fig. 1). The voltages expressed in this report were referred to sat. Ag/AgCl (+0.197V *vs.* SHE). The enzymatic cathode (geometric area 2.25 cm^2) was prepared as described previously.[5] The electrolyte used was phosphate buffer solution (PBS, 100 mM) with or without the addition of activated sludge (AS, 40ml). The AS was used as bacterial/pollutants source to evaluate the enzymatic degradation due to bacterial contamination. The cathodes were poised at 0.3V for the first two days, 0.2V during the following two days, and 0.1V in the remaining time of the tests.

At the beginning, the OCPs were slightly higher than 0.5 V for the PBS solution and the PBS/AS solution (Fig. 2a), as previously showed.[5] Over time the OCPs decreased and after 12 days, the cathode facing PBS had an OCP of 0.415 V while the one in the PBS/AS solution had a low OCP (0.3 V), which was the typical OCP achieved by the material only without enzymes addition, underlining the probable complete deactivation/ poisoning of the enzymes. At the same time, the current density generated at a constant potential of 0.25V showed the advantage of the cathode performance in absence of bacteria (Fig. 2a). The enzymatic activity decreased much faster in the presence of bacteria/pollutants in the AS solution. The current generated on day 12 was still relatively high (≈200 μA/cm^2) in the PBS solution and but was only ≈50 μA/cm^2 in the PBS/AS solution (Fig. 2a).

A general view of the cathode's performance over time was showed by the polarization curves, with two arrows pointing the decrease of OCP and current (Fig. 2b). The presence of bacteria/ pollutants in the PBS/AS solution lowered the current output and reduced the enzymatic activity faster than the natural occurring deactivation in the PBS solution. The interaction between bacteria/pollutants and enzymes, and the enzymes protection (*e.g.*, silica encapsulation) to prolong the lifetime of BOx based cathodes should be further investigated for more practical applications.

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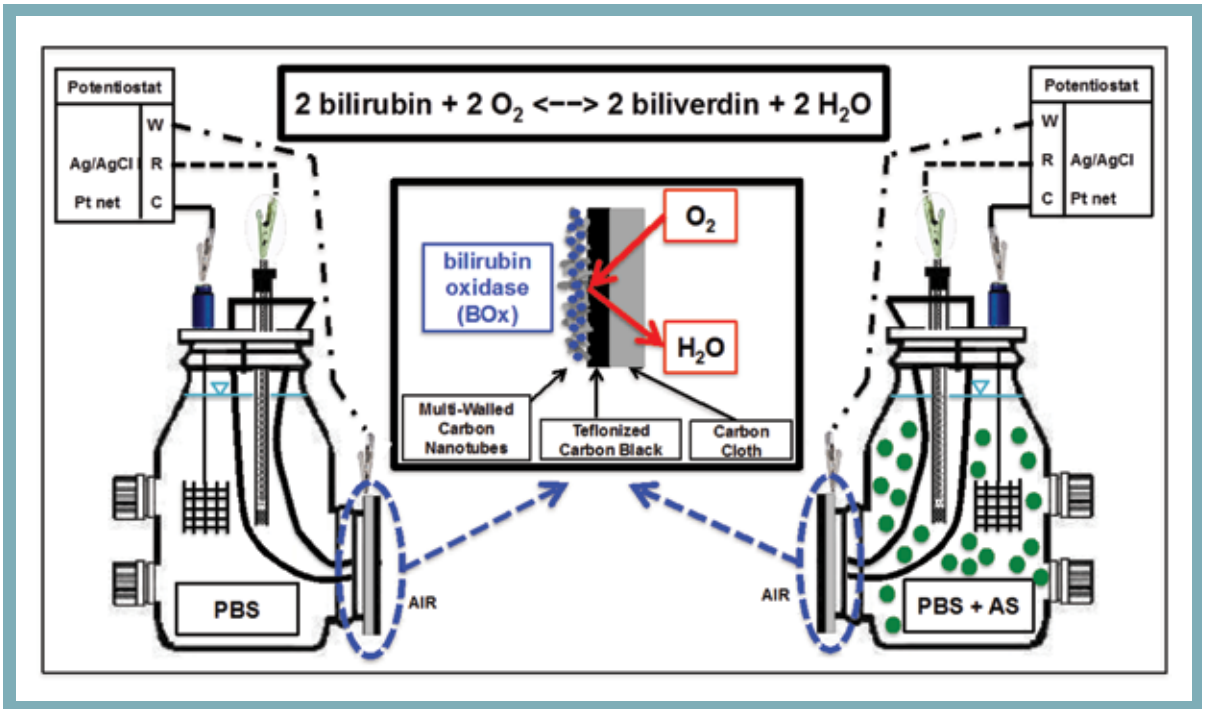

FIG 1. *The half electrochemical cell configuration and cathode detailed design.*

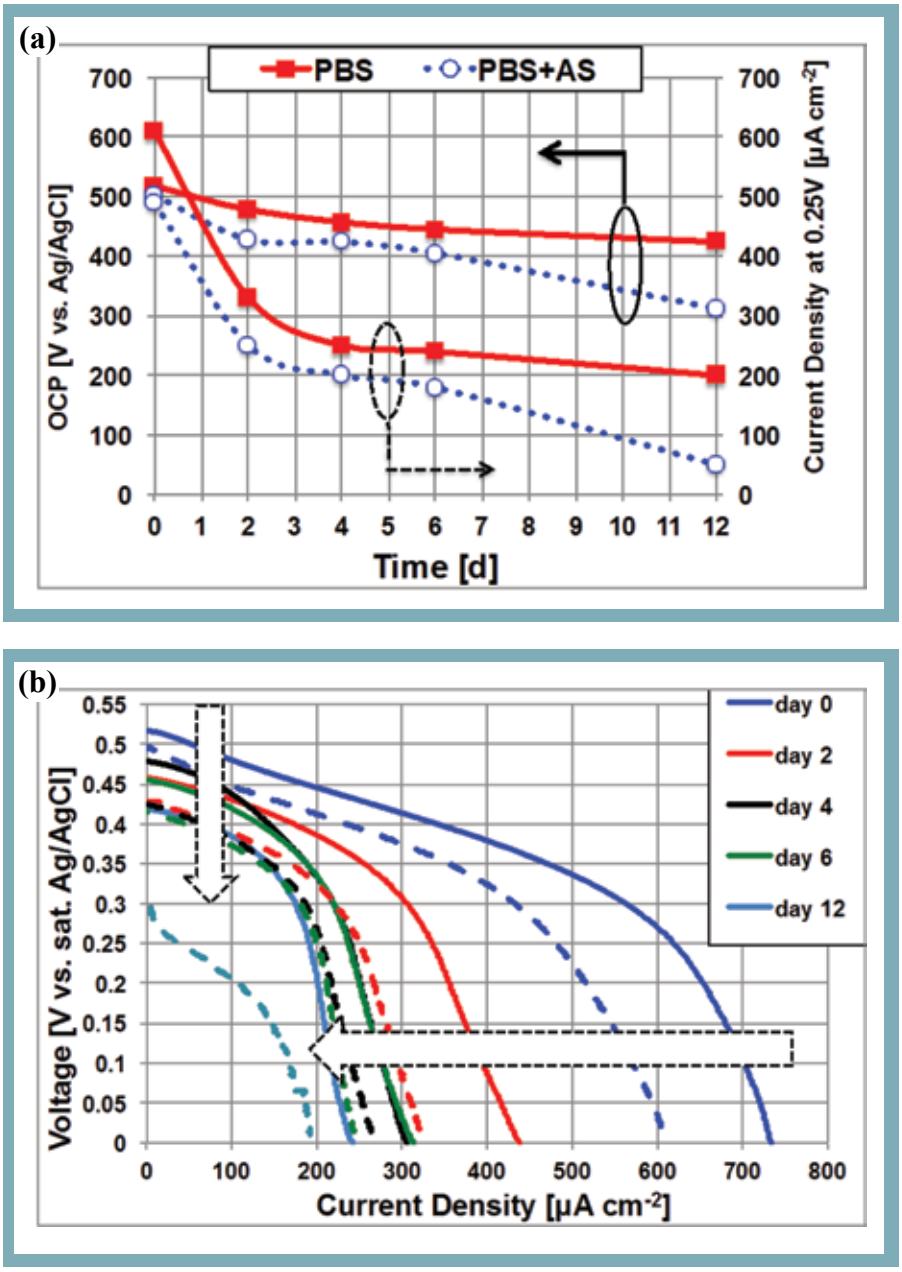

Fig. 2. *The trend of OCP and current density during a 12-day test period (a). The changes of polarization curves during a 12-day test (b). (Solid line indicates the PBS solution, and broken line indicates the presence of bacteria in the PBS/AS solution).*

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Carlo Santoro is a PhD candidate in the Department of Civil and Environmental Engineering at the University of Connecticut. He is pursuing his degree under the guidance of Baikun Li in the School of Engineering. His thesis concentrates on the optimization of the cathode in microbial fuel cells and particularly the improvement of the cathode structure, the decrease of catalyst loading, and the study of platinum-free cathodes (*e.g.* biocathodes and enzymatic-based cathodes). He may be reached at carlo.santoro830@gmail.com.

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