Doctoral Dissertation
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Design, characterization and modelling of electrodes and structures for Bio-Electrochemical devices

By

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Abstract

The research on Bio-Electrochemical Systems (BES) is characterised by a multidisciplinary approach involving biotechnology, chemistry and materials science aspects. All of them are characterised by phenomena that are worth investigating with tools and perspectives drawn from the field of physics. This thesis investigates critical aspects in the operation of BES through a physics-oriented approach, with the aim of contributing to the BES technology. In this work, three main aspects of BES operation are taken into account. The first aspect is related to the cathodic oxygen reduction reaction (ORR), which characterises both biotic and abiotic fuel cells. With a focus on environmental and economical sustainability, it is recognised how the ORR can be catalysed by non-precious materials alternative to platinum. Among them, manganese oxides are among the most promising solutions and are the subject of this study. Moreover, possible strategies to enhance the ORR activity of a catalyst are identified in nanostructuration and in the introduction of oxygen vacancies. With a view to realising cathode electrodes featuring the aforementioned characteristics, this thesis analyses a technique to promote the formation of a specific manganese oxide phase which is more active towards ORR. Starting from a manganese oxide precursor, this selectivity is achieved by tuning the oxygen exposure during precursor calcination. In addition, the use of electrospray technique for the deposition of the manganese oxide precursor demonstrates the possibility to synthesise a nanostructured manganese oxide-based catalyst layer directly onto the electrode surface. The hypothesis on the formation of a specific phase, based on manganese oxide stability model, is verified via spectroscopic (Raman, X-ray) and diffractometric (X-ray) techniques that provide information on crystallinity and on surface chemistry properties of the catalyst material. A final validation step, performed in an electrochemical setup characterised by an alkaline environment, demonstrates the ORR catalytic activity achieved by the cathodes realised in this work. The possibility to develop a catalyst layer featuring the most ORR-active phases of manganese oxide provides the basis for the development of future noble-metals-free cathodes of biotic and abiotic fuel cells. The second aspect of BES operation considered in this thesis concerns the enhancement of the charge transfer processes occurring at the anodic abiotic-biotic interface. Carbon-based materials are usually employed to realise the anode electrode, which needs to satisfy a series of conditions in order to develop an efficient interface with the electroactive biofilm. Among these, key factors are the electrical conductivity of such interface and the electrode surface wettability. To address the electrical conductivity and wettability aspects, this work proposes the enhancement of commercial carbon-based electrodes via a surface deposition of an intrinsically conductive polymer (PEDOT:PSS). By performing this deposition via the ultrasonic spray coating technique, a nanostructured layer containing a controlled amount of polymer is deposited on the surface of carbon paper. The impact of the deposited layer on electrical conductivity is assessed by analysing, via Raman spectroscopy, the polymer chain conformation induced after the deposition process. Such conformation is known to affect the spatial arrangement of the polymer chains inside the conductive layer and, consequently, its electrical conductivity. Instead, the impact on wettability of the deposited layer is analysed in terms of electrochemical active surface area enhancement, for which an expected trend model is presented. Finally, the effects on electrical performances and on charge transfer processes occurring at the anodic abiotic-biotic interface is assessed via electrochemical impedance spectroscopy in a lab-scale BES validation experiment. The final aspect of BES operation investigated in this thesis deals with the analysis of the electrolyte fluid-dynamics occurring inside BES. The undesirable phenomena of biofouling and of cathode-to-anode oxygen cross-over relate to the BES electrolyte chamber and negatively affect overall device performances. To mitigate these effects this work proposes an innovative microfluidic-based approach, based on the modification of the internal design of single chamber microbial fuel cells. Such modification is achieved via the insertion of a custom-designed intermediate microfluidic septum (IMS) inside the electrolyte chamber. The impact of the IMS design on electrolyte fluid dynamics is studied via finite-elements computational simulations, focusing on the effect of the IMS on diffusive and convective processes occurring inside the BES. The advantages expected from the IMS design are then validated in a lab-scale BES experiment, which allows to correlate the presence of the IMS with effects on charge transport processes at internal interfaces and with enhanced electrical performances.