

Modified Carbon Electrodes: A New Approach for Bioelectrochemical Systems

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The development of sustainable and green technologies for the treatment and recovery of resources from wastes is driving a paradigm shift in waste management. Bioenergy production from waste streams can lead to the reduction of pollution, but also decrease the cost of their treatment. Among the new environmental friendly technologies, microbial bioelectrochemical systems (BESs), like microbial fuel cell (MFC) [1] or microbial electrolysis cell (MEC) [2], are considered one of the best alternatives for the sustainable waste treatment of contaminated groundwater [3], wastewater [4] and air polluted streams, and the concomitant production of energy or added value chemicals. [5] One of the critical challenges of these systems is to improve the interaction electrode-microorganism to ensure an effective transfer of electrons between the solid-state electrode and the biocatalyst. Carbon and graphene materials with various structures, shapes and properties are widely used as electrodes for BES applications due to their high conductivity, good chemical stability and relatively low cost [6,7] However, the performance of BES is often hindered by low currents and mass transport limitations. A major challenge in this context is an increase in the performance by decreasing the high overpotentials of such systems. Puig et al. [8] identified these overpotentials as the main energy loss factors (83- 90 % of total losses) in an autotrophic denitrification in MFCs for waters with low ionic strengths. In this respect, current research is focused on studying the effects of surface chemistry and the porosity of carbons on their performance in one electrode reaction in BES [9]. The new capabilities of the design, preparations and techniques in material sciences raise the question if BES can benefit from these developments and their performance can be increased further more.

Biofilms on electrode surfaces play a key role in current generation or transformation in BES. By modifying the electrode properties the electronic conductivity, electron transfer and biofilm adhesion can be enhanced. These modifications include (1) an increase of the porosity for the most effective utilization of the surface area [10]; (2) the presence of surface functional groups such as oxygen [11] and nitrogen [12]; (3) an increase of the conductivity and (4) biocompatibility [13]. The surface properties, which include the chemistry and charges present at the electrode surface, have been found to affect bacterial adhesion, biofilm formation and electron transfer significantly [14]. In this regard, one strategy is the improvement of the electrode surface properties by surface treatment procedures such as ammonia treatment, polymer modification or surface oxidation [12]. Recent reports have demonstrated an increase in the current density by the presence of oxygen and nitrogen functional groups at the electrode surface of carbon paper or carbon cloth, graphite felt or brush or reticulated vitreous carbons [11,15]. These surface modifications are likely to improve biofilm-electrode interactions and thus the rate of electron transfer. Nevertheless, despite numerous studies, the role of the carbon surface features in BES is yet to be clearly established.

A further, promising path is the increase of the active surface area of the electrode material. Substantial current research on porous materials focuses on the development of methods for the generation of functional porous solids with tailored pore structures and pore

topologies. Especially interesting are hierarchical porous materials which consist of a combination of mesopores (between 2 - 50 nm) and macropores (width larger than 50 nm), and graphitic degree [16]. Among those three-dimensional materials, carbon sponges, fibers and aerogels have demonstrated an increase of current density of up to 6.8 mA cm⁻², and fatty volatile acids production such as formic acids and acetate. Very recently porous carbon electrodes containing carbon nanotubes (CNTs) have brought considerable attention due to the combination of high surface area, enhancing the biofilm growth and the current density generated and the high conductivity of the CNTs [17,18].

To provide novel properties, the design of new electrodes combining surface chemistry and porosity remain crucial for new generation BES. The electrode material is a key component that determines a BES performance and the most definitive test for a new electrode material is how it performs in a full scale, commercial system. However, for that the mechanistic understanding of the interaction between microbes and such modified electrodes is still needed.

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