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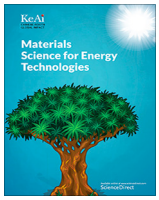

Application of silver-tin dioxide composite cathode catalyst for enhancing performance of microbial desalination cell

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ABSTRACT

Microbial desalination cell (MDC) is a novel bioelectrochemical system, capable of removing salts and organic matter from wastewater simultaneously. For improving the performance, a carbon supported silver-tin dioxide (Ag-SnO_2) composite was synthesized and used as cathode catalyst in a five-chambered MDC (MDC-1). The results were compared with MDC-2 having no catalyst on the cathode. Saline water with a NaCl concentration of 20 g/L was used to evaluate the desalination efficiency of both the MDCs. The electrochemical studies such as cyclic voltammetry and linear sweep voltammetry of the cathode of MDC-1 revealed the superior reduction kinetics. Increased desalination efficiency was observed in MDC-1 (72.6 ± 3.0%) due to presence of Ag-SnO_2 catalyst as compared to MDC-2 (57.9 ± 8.6%). Maximum power density of 1.47 W/m^3, demonstrated by MDC-1, was noted to be 1.67 times higher than that of MDC-2 (0.88 W/m^3). In addition, the coulombic efficiency of MDC-1 was observed to be 14.4 ± 0.2%, which was significantly higher than that observed in MDC-2 (9.5 ± 0.3%). Performance results confirmed the excellent catalytic activity of Ag-SnO_2 composite catalyst to be used on the cathode of MDCs, to take forward this cutting-edge technology for field scale application.

1. Introduction

Increasing population of the world is the main reason behind the depletion of the fresh water sources and its pollution, which is the major concern for human civilization. In addition, the distribution of water is another challenging issue due to the difference in availability of fresh water sources across the regions. The uneven distribution of water in the world provoked the development of sustainable technologies to produce quality water to fulfil the growing demand for water. Long-term solution to this increasing water demand can be obtained by seawater or brackish water desalination [1]. On the other hand, the energy consumption for the water treatment is growing at a faster rate resulting in increased costs for fresh water supply, which possesses a huge demand for developing a combined reactor that can desalinate seawater or brackish water and produce power simultaneously. This can be achieved through the application of bioelectrochemical system (BES), which is an integrated system combining wastewater treatment with energy generation and in-situ resource recovery [2]. A microbial fuel cell (MFC) is a typical example of BES, which employs microbes as bio-catalysts to treat wastewater and produce electricity simultaneously [3].

Microbial desalination cells (MDCs) are modified form of MFCs that facilitate in-situ desalination of saline water with valuable energy recovery [4]. MDC is considered as a promising technology, which can alone treat saline water or act as a pre-treatment device for reverse osmosis (RO) to enhance the service life of RO membranes [5]. In the anodic chamber of MDC, the organic matter present in wastewater is oxidised by electrochemically active microorganisms, thus producing electrons, protons and CO_2. The electrons travel from anode to cathode via external conductive wire and reduce a terminal electron acceptor (TEA), such as oxygen [6], ferricyanide [7] etc. The reverse polarity of electrodes in this system creates a natural redox gradient for successfully accomplishing the migration of ions from the middle desalination chamber of MDCs, facilitating salt removal [8]. As a result of remarkable benefits, the recent years have seen outstanding research focused on the structural and functional optimization of MDCs to improve its desalination efficiency for field scale applications [9].

The cathodic reduction reaction, for example, oxygen reduction reaction (ORR) is the major constituent, which affects the performance of MDCs. Thus, the foremost challenge is to develop a stable and efficient catalyst to enhance the reduction reaction

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at the cathode. Due to abundant availability, sustainability and high redox potential, oxygen is preferred as an ideal terminal electron acceptor and the ORR is the most preferred reaction in BES. However, due to the sluggish kinetics of the ORR, the MDC experiences high overpotential losses [10], resulting in decreased overall system performance. Studies were conducted using oxygen as a TEA along with platinum (Pt) as catalyst to reduce the ORR overpotential. While using equal volume of anodic solution and saline water, MDC using air cathode with platinum catalyst has achieved desalination efficiency of 43% and 67% from saline water with NaCl concentrations of 5 g/L and 20 g/L, respectively [11].

An up-flow microbial desalination cell (UMDC) with air cathode was fabricated by Jacobson et al. [12] for continuous mode of operation for the purpose of salt removal from saline water. This UMDC was able to demonstrate salt removal of more than 99% with an initial salt concentration of 30 g/L in saline water [12]. Maximum total desalination rate of 0.025 g/h was achieved with platinum-catalysed stacked MDC, which was 1.4 times higher than a single chamber MDC with Pt catalyst on the cathode [13]. However, platinum cannot be used in larger MDCs because of its high cost and instability due to sulphide poisoning [14]. Subsequently, extensive research has explored novel, durable, highly active and affordable substitute for platinum-based materials over the past decades [14,15].

Tin dioxide (SnO_2) has engrossed increasing attention as an important metal oxide because of its wide range of applications in optoelectronic devices and dye-sensitized solar cells [16]. Recently, the synthesis of nanocomposites by combining SnO_2 with noble metals has received noteworthy attention. A solution-based method was used to prepare Au–SnO_2 nanostructures and further their photocatalytic activity was tested [17]. The results revealed the exceptional photocatalytic activity of Au anchored with SnO_2 due to increased charge-transfer efficiency. On the other hand, Silver nanoparticles (Ag-NPs) have diverse properties like antibacterial, physico-chemically stable for the lasting applications and also found to possess elevated ORR activity. In addition, it was demonstrated as an excellent electrochemical catalyst for ORR at alkaline medium [18]. Earlier 5% Ag-NPs in carbon powder was used as cathode catalyst in MFC. Using this catalyst, a power density was improved by 4.6 folds when compared to MFC with no catalyst on cathode and it also inhibited fungal bio-fouling on cathode for supporting long-lasting operation of MFC. Thus, the use of Ag-NPs as cathode catalyst could improve the performance of system [19].

In the present study, SnO_2 was anchored with silver nanoparticles (AgNPs) to make Ag-SnO_2 composite and it was explored as a cathode catalyst on carbon support in MDC to increase the desalination efficiency and to improve the coulombic efficiency (CE). As synthesized Ag-SnO_2 composite was physically characterized by X-ray diffraction technique (XRD) and transmission electron microscopy (TEM) to evaluate the lattice parameters and phase orientation. Electrochemical analyses such as cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were used to evaluate the ORR kinetics of cathodes, one containing Ag-SnO_2 and the other one with only carbon. The performance results of MDC with Ag-SnO_2 catalyst on cathode were compared with the results obtained from MDC with no catalyst on the cathode in terms of desalination efficiency, power recovery and CE.

2. Materials and methods

2.1. Tin dioxide synthesis by sol-gel method

Tin dioxide was prepared by a simple sol-gel method using tin chloride ($SnCl_2$) and oxalic acid ($C_2H_2O_4$) as precursors [20]. Oxalic acid was used as reducing agent in this process. A solution of 0.5 M of $SnCl_2$ was prepared in 150 mL of de-ionised (DI) water and it was kept for stirring at 60 °C on a hot plate stirrer. After 15 min of continuous stirring, 250 mL of 0.75 M oxalic acid was added drop by drop to the solution and stirred for one more hour for complete reduction. White coloured semi-fluid crystals were then formed, which indicated the growth of tin oxalates in nanometric dimension. The resultant crystals were separated by filtration and then washed with ethanol to remove impurities and oven dried at 100 °C for two hours. The dried materials were subjected to calcination at 400 °C in a muffle furnace (ThermoFisher Scientific, India) under air for three hours, which resulted in the formation of gray coloured tin dioxide (SnO_2) loose powder. As-synthesised SnO_2 powder was then stored in air-tight container for further use.

2.2. Preparation of Ag-NPs

Silver nanoparticles (Ag-NPs) were prepared by the reduction of colloidal silver chloride solution using hydrothermal process [19]. In this reduction process, 0.02 M (5 mL) of silver nitrate ($AgNO_3$) and 0.02 M (5 mL) of sodium chloride (NaCl) were mixed together in 30 mL of DI water under vigorous stirring condition. Dextrose (0.04 g) was added to the solution as reducing agent and stirred for two to three minutes in magnetic stirrer (REMI, India). The resultant solution was transferred to Teflon lined autoclave and kept in a muffle furnace at 180 °C for 18 h. The fluffy gray precipitate was recovered by centrifuging at 5000 rpm (REMI, India) and washed with both DI water and ethanol to remove all the chloride ions and other contaminants from the precipitate. Recovered Ag nanoparticles were dried in a hot-air oven at 100 °C and finally stored in an air-tight desiccator [19].

2.3. Preparation of cathodes

Carbon felt was used for fabrication of catalysed cathode. The ink-based electrocatalyst composite solution was prepared by mixing of 1 mg/cm^2 as-synthesized SnO_2 and 0.05 mg/cm^2 Ag-NPs (maintaining 5% weight of SnO_2) on the support of 1 mg/cm^2 Vulcan XC carbon powder. Polydimethylsiloxane (PDMS), having a loading rate of 33.3 μL/cm^2 was used as a binder for the composite material in 30 mL acetone, which acted as a solvent [3]. The weight of catalyst materials was normalized based on geometric surface area of the cathode. The details of composition and the amount of materials used to make electrocatalyst ink are furnished in Table 1. The above catalyst mixture was sonicated for 30 min in a high-frequency sound wave processor (Piezo-U-Sonic, India) operated at 120 kHz to obtain a homogenous composite catalyst solution. A piece of clean carbon felt, cleaned by immersion in 1 N HCl for one hour, with a projected surface area of 27 cm^2 was wet-coated with the resultant conductive ink using a sprayer operated with highly pure compressed N_2 gas. The fabricated cathode was dried in hot air oven at 100 °C and stored in

Table 1
The composition and the amount of materials used to make electrocatalyst ink.

S. No.	Components in electrocatalyst solution	Amount (loading rate, mg/cm^2 of cathode surface*)
1	SnO_2	1
2	Vulcan XC carbon powder	1
3	Ag-NPs	0.05 (5% by weight of SnO_2)
4	Polydimethylsiloxane as binder	33.3 μL/cm^2
5	Acetone as solvent	30 mL

* Otherwise stated.