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Co^{3+} homogeneous mediator generation efficiency in a divided tubular electrochemical reactor with MFI-type zeolite membrane

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ABSTRACT

In the present work a tubular electrochemical cell with MFI-type zeolite coated membrane (TZM) was engineered and evaluated using Co^{2+} oxidation efficiency in high acid medium. Electrolysis of Co^{2+} was carried out at room temperature ($20 \pm 3\,^{\circ}$C) in 4 M H_2SO_4 at anodic half-cell, and showed 42% Co^{2+} oxidation with 0.3 V higher cell voltage than the commonly used Nafion324 membrane in planar arrangement. Further, the TZM membrane was robust when operated in the cell at different temperatures (10, 30 and 50 °C) as no noticeable change in surface morphology was observable by SEM analysis. Further testing showed Co^{2+} oxidation efficiency decreased with temperature and increased with current density, suggesting stable operation of the TZM but structural change in cobalt precursor. The TZM membrane showed less resistance 0.91 Ω cm^2 (at 10 °C) than Nafion324, which is decreased with increasing temperature from 10 °C to 50 °C. A 72 h test of the TZM at slightly elevated current density (70 mA cm^2) showed increased oxidation efficiency of Co^{2+} to 57% compared to the traditional planar cell with Nafion324 (43%). Therefore, the engineered tubular electrochemical reactor with TZM is robust for generation of homogeneous mediators towards environmental pollution removal.

Introduction

The electrochemical removal processes show promising performance in an environmental liquid or gaseous pollutant removal processes. Membranes which divide the electrochemical cell play a crucial role in generation of active mediators [1,2] and separate the product formed during paired electrolysis [3–5]. In generation of mediators, Nafion membranes are effective separators, which are also used in generating oxidative mediators such as Ce^{4+}, Ag^{2+} and Co^{3+} in acid medium [6–8]. In a similar way, reductive mediators such as Ni^{1+} and Co^{1+} have been generated by paired electrolysis using Nafion membrane [9,10]. In the chloralkali process, chlorine and Na^{1+} have been recovered by cells installed with Nafion membranes [11]. Planar Nafion 'plate and frame' arrangements have been used to divide the cell allowing voltage and current efficiencies, as well as durable operation [12,13]. However, the tubular continuous flow electrochemical reactor has been identified as having an effective volumetric conversion capability compared to other flow reactors [14,15]. Continuous flow in undivided cylindrical cell has been modelled by finite element method (FEM), resident time distribution (RTD), and computational fluid dynamics (CFD). The modelling supported further consideration towards industrial tubular reactor development [16–18]. As a result, experimental analyses of undivided tubular reactors have been conducted at laboratory and industrial scale for water treatment [19–21]. However, electrode contamination occurs on systems that are applied to environmental applications due to the diverse array of chemical components in aqueous and gaseous wastes. To address this issue, tubular electrochemical reactors with self-cleaning function using TiO_2 in porous carbon conductive electrode has been developed for industrial waste water treatment [22,23]. In the field of organic synthesis such as propanol, an undivided tubular cell has been established using Ti with carbon anode and SS cathode [24].

In order to further improve the performance of cylindrical electrochemical reactors, a divided tubular electrochemical cell would be an added advantage. The membrane that used to dividing the electrochemical cell sections must have high mechanical and chemical stability in order to operate under diverse temperature, pH and contaminant regimes. Ceramic membranes, made

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commonly of oxides of aluminium, titanium, silicon, or zirconium, are mechanically, thermally and chemically robust. Advanced coated types provide precise size exclusion functionality over their long service life due to their ability to be easily cleaned without deteriorating their performance [25–28]. More specifically, they are highly stable in severe acidic and alkaline media and resistant to oxidants [29,30]. As an anode, tubular ceramic membrane modified using metal or carbonate effectively captured the greenhouse gas CO_2 from flue gas [31]. For waste water treatment, cross flow electro-filtration using AlO_2/TiO_2 [32] and pyrolytic carbon deposited electro-conductive [33] microporous ceramic tubular membranes have shown promising performance. For energy application, porous Vycor glass (silica glass) with 4.5 nm pore size was applied as a tubular divider for all vanadium redox flow battery applications [34].

Commercial ceramic membrane pore sizes range between 0.005 μm and 50 μm [35], which may facilitate good ionic and electric conductivity, but the pore size is too large to prevent mediator ions migrating to the other half cell, reducing the oxidation/reduction efficiency of the mediator. Planar ceramic membranes with different pore sizes were analysed for electrical conductivity in a basic three electrode system to assess their viability as a cell dividing membrane and found electrical conductivity factor of $0.35\ \varepsilon^{1.04}$ [35]. Ideal separators to divide the cell should possess [36]:

1. high electric passage with no permeation of molecular species;
2. minimized ohmic drop or maximize the effective electrical conductivity; and
3. uniform current distributions for high current efficiency.

With these, often a compromise is made between the demands for effective separation of anodic and cathodic compartments and the cell voltage that must be attained.

A type of ceramic membrane that has pore size needed to retain ionic species, being <1 nm, is a zeolite membrane. Zeolite coated ceramic membranes have been applied for gas and liquid separation [37–39] and membrane reactors [40] due to their molecular scale pore size for high separation performance, as well as high thermal, chemical and mechanical stability [41,42]. Ionic and small molecule retention by zeolite membranes is achieved by the crystalline structure, often in the form of the MFI-type zeolite, which has an intrinsic pore size of 0.56 nm [43]. This comes from orthorhombic crystal symmetry of nearly cylindrical 10 member ring channels [44], which enables water transport (and protons) but rejection of the other molecules. Using this small pore size, hydrated ions with sizes starting from K^+ (0.662 nm) and Cl^- (0.664 nm), can be separated from much smaller water molecules (kinetic diameter is 0.276 nm [45]). MFI-type zeolite membranes have also been explored for redox flow battery application demonstrating their ion rejecting/proton passage property, long life and high stability in the electrochemical field [46]. Tubular MFI-zeolite coated membranes made by seed rubbing and secondary growth were shown to desalinate synthetic NaCl solutions and real saline waste water [47,48]. By providing hydraulic pressure above the osmotic pressure as driving force for water molecules, water permeated through the zeolite membrane while rejection of the metal ions Ca^{2+} and Mg^{2+} was >90% and Na^+ and K^+ was >70%, and waste water organic rejection was >90% [47,48]. Other work on simulated produced water showed 99.5% organic rejection by MFI-type zeolite membrane [49,50]. With these promising results in passive and active filtration, there appears to be great potential for zeolite membranes for mediator ion retention and proton passage in electrochemical oxidation. Hence, our aim in this work was to consider the novel potential for tubular MFI-type zeolite coated ceramic membranes as a divider in development of tubular electrochemical reactor for electrochemical generation of homogeneous oxidant mediator. The TZM efficiency was analysed by Co^{2+} oxidation with varying temperature, current density, and electrolyte flow rate. TZM stability was studied by Co^{2+} migration and cell potential variation, and compared with the results of the commonly used Nafion 324 in plate and frame electrochemical cell as a reference.

Experimental

Materials

Cobalt sulfate ($CoSO_4{\cdot}7H_2O$, 99.9%) and sulfuric acid (H_2SO_4, 60%) from Sam Chun Chemicals, Korea, and ferrous sulfate ($FeSO_4{\cdot}7H_2O$) from Junsei Chemical Co., Ltd, Japan were used as received without any further purification. For MFI-type zeolite coating, 1 M tetra-propyl ammonium hydroxide (TPAOH) solution, sodium hydroxide pellets (NaOH, 99.99%), fumed silica (SiO_2, particle size 0.014 mm, surface area $200 \pm 25\ m^2\ g^{-1}$) and tetraethyl orthosilicate (TEOS) (98%) were purchased from Aldrich. A tubular ceramic support α-Al_2O_3 (~31 vol % porosity, diameter (ID: 2.54 cm, OD: 3.2 cm), thickness 0.24 cm, length 14.5 cm, ~0.11 μm nominal pore size) was supplied by Chosun Refractories Co. Ltd, Korea. The continuous flow type tubular cell with an option for tubular membrane used in the present work was engineered using high quality PVC with Viton gaskets in our laboratory specifically for the tubular membrane specifications.

MFI-zeolite coating method

A secondary growth technique was used to coat the ceramic supports, which involved rubbing silicalite seeds on the ceramic tubular support followed by growth of the membrane under hydrothermal conditions as reported elsewhere [46,47]. The method involved hydrothermal secondary growth which was carried out in a growth solution of 20 mL of 1 M TPAOH, 20 mL of TEOS and 360 mL deionized water at 180 °C for 16 h. After growth, the membrane was washed in deionized water to remove loose precipitate and was then calcined at 500 °C for 4 h. The MFI zeolite (silicalite) seeds were prepared by calcining the silicalite suspension at 525 °C for 6 h with a temperature increase/decrease rate of $1\ ^\circ C\ min^{-1}$ to remove the organic template from the zeolite frame work. The silicalite suspension was synthesized from a solution of 43 mL of 1 M TPAOH, 0.6 g NaOH and 8.5 g fumed silica using a hydrothermal process [30] at 180 °C for 8 h. The hydrothermal synthesized suspension was thoroughly washed with deionized water by repeating centrifugation and re-dispersion in deionized water four times prior to calcination.

To eliminate possible defects in membrane, the prepared zeolite membrane underwent a post-synthetic treatment by a novel ion infiltration method prior to electrochemical oxidation testing. In brief, ion infiltration was performed using pressurized filtration of the ion solution containing Fe^{3+} ($4750\ mg\ L^{-1}$), Al^{3+} ($6000\ mg\ L^{-1}$), Ca^{2+} ($150\ mg\ L^{-1}$), Mg^{2+} ($9500\ mg\ L^{-1}$) through the zeolite membrane in a similar test system used for desalination. The membrane was installed into the stainless steel membrane housing, and the ion solution was fed at a flow rate of $5\ mL\ min^{-1}$ by a high pressure piston pump (Series 1, LabAlliance, USA) in a cross-flow setup with the feed solution fed under pressure (1 MPa) on the outside and permeating to the inside of the membrane. The desalination performance after defect repair by the ion infiltration was evaluated by measuring rejection of NaCl solution ($3000\ mg\ L^{-1}$ TDS) using a similar desalination test rig described elsewhere at an applied pressure of 0.5 MPa and 21 °C [51]. The defect repaired zeolite membrane showed improved salt rejection (24% increased to 84%) which was close to that previous reported for zeolite desalination membranes (~90% salt rejections) [49,51]. The high NaCl rejection demonstrates the ability for the membrane to retain larger cobalt and sulphate ions

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