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Anionic catalyst binders based on trimethylamine-quaternized poly(2,6-dimethyl-1,4-phenylene oxide) for alkaline electrolyzers



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ABSTRACT

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was brominated under the conditions of radical mechanism and subsequently quaternized with trimethylamine. Flat membranes were prepared by casting quaternized PPO (qPPO) dissolved in ethanol or ethanol/dimethylformamide mixture on a Teflon plate followed by solvent evaporation. The membranes were characterized by their degree of swelling in water, ion exchange capacities (IEC) and ionic conductivities. qPPO with a degree of quaternization of 25.5 mol% and with anionic conductivities of 10.09 S/m and 12.34 S/m (at 50 °C and 70 °C, respectively) was tested as an anion-conductive polymer binder in a single cell alkaline laboratory electrolyzer in which the anode and cathode compartments were separated with a heterogeneous anion selective membrane. The cathode contained Pt/carbon catalyst bonded with qPPO so that Pt/qPPO weight ratio was 85/15. The anode contained NiCo₂O₄ spinel catalyst which was bonded either with qPPO (spinel/qPPO weight ratios 95/5, 90/10 or 75/25) or with a non-conducting PTFE (spinel/PTFE weight ratio 85/15). It was found that the application of the qPPO binder in the anode lead to higher current densities than the application of a non-conductive PTFE binder at all electrolyte KOH concentrations (1–15 wt%). The performance of a laboratory membrane electrolyzer with the anode containing NiCo₂O₄ spinel catalyst bonded with qPPO (spinel/qPPO weight ratio 75/25) and a 1 wt% KOH electrolyte was similar to that of an industry unit with a 30 wt% KOH electrolyte.

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1. Introduction

Water electrolysis may represent a key technology of hydrogen production, especially when surplus electricity from renewable sources, such as photovoltaics and wind turbines is used. The produced hydrogen may be stored and used later in chemical industry (e.g., in petrochemical industry or in ammonia production) or its energy may be used for electricity generation, e.g. in fuel cells. The second way is preferred due to the purity of produced hydrogen and the fact that hydrogen for industrial use coming from natural gas steam reforming is significantly cheaper and currently available in sufficient quantities.

Three main processes of electrolytic decomposition of water are available:

- (i) High-temperature steam electrolysis is under development. It has gained much interest as the process involves less electrical energy consumption compared to the conventional

low-temperature water electrolysis. However, this technology still suffers from material issues.

- (ii) Proton exchange membrane (PEM) electrolysis is an established technology (though only on a relatively small scale) despite the fact, that this technology achieves high voltage efficiency and intensity of production. A PEM electrolyzer cell is similar to a PEM fuel cell, just the principle of its operation is reverse. It uses principally the same perfluorosulfonic acid membranes, the same expensive noble metal catalysts and only carbon materials (catalyst support, porous electrode structures and bi-polar plates) have to be replaced with metallic parts due to corrosion. A more widespread use of PEM electrolyzer technology would create a growing demand for noble metals but the supply of noble metals is limited.
- (iii) Alkaline water electrolysis is the only one that is industrially used. It employs an aqueous alkaline solution as an electrolyte. The process has two major disadvantages: the uses of carcinogenic asbestos as diaphragms and of highly concentrated (25–30%) potassium hydroxide as an electrolyte.

An alternative to alkaline water electrolyzers and PEM electrolyzers may be anion-exchange membrane (AEM) electrolyzers. AEM

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electrolyzers rely on a polymer anion-exchange membrane instead of asbestos or another inorganic diaphragm. The advantages of AEM electrolyzers over PEM electrolyzers consist in the use of cheap catalysts (the catalysts may be based on non-noble metals or their oxides) and in good corrosion resistance of supporting materials in alkaline environments. The problems of AEM electrolyzers are anion-exchange membranes, which are usually less conductive and less stable than their cation-exchange counterparts, and the use of anionic polymer binders.

In AEM electrolyzers (or in alkaline fuel cells), a polymer binder is needed to fix discrete catalyst particles to the electrodes. The resulting catalyst layer should form a three-phase boundary that simultaneously allows the transport of hydroxide ions, electrons, and reactants/products. Current alkaline fuel cells usually rely on binders based on poly(tetrafluoroethylene) (PTFE) [1–3]. PTFE is a highly stable polymer forming an advantageous microporous structure on catalyst particles. As it is, however, not anion conductive, alkaline fuel cells and electrolyzers with PTFE binder have to rely on KOH or NaOH liquid electrolytes. It would be advantageous if the electrolyser (or cell) medium was pure water rather than an alkaline electrolyte since most anion-exchange membranes are not stable enough in a high pH environment at increased temperatures. Therefore, it is desirable to replace electrically neutral PTFE with hydroxide ions conductive ionomer. This ionomer, besides being hydroxide ions conductive, must be reasonably stable in the electrolyser or fuel cell environment, it should not swell excessively in water (and thus block the pores for the transport of reactants and products) and it should be soluble in low-boiling point solvents (such as ethanol or propanol) because these solvents are safe to handle and easy to remove during the electrode preparation. Some anionic binders have been already prepared and tested in alkaline fuel cells and electrolyzers.

Valade et al. [4] replaced part of the Cl^- counter-ions in water-soluble poly(diallyldimethylammonium chloride) with bistrifluoromethanesulfonimide ions (TFSI^-). The products were water-insoluble but films could be cast from their dimethylsulfoxide solutions. After immersion of the films into an aqueous sodium hydroxide solution, the remaining Cl^- counter-ions were replaced with OH^- anions, but no replacement of the TFSI^- anions occurred. When the products were used in a solid alkaline fuel cell as binders, significant improvements in the open circuit voltage, current density and accessible power were noted.

Zhang et al. [5] synthesized an anionic ionomer by grafting of poly(vinylidene fluoride) with poly(vinylbenzyltrimethylammonium chloride). The electrodes for a direct hydrazine hydrate fuel cell were prepared by spraying a carbon cloth with a catalyst ink comprising a dispersion of catalyst particles in the solution of prepared anionic ionomer or in the solution of unmodified poly(vinylidene fluoride). A commercial anion-exchange membrane (Tokuyama Co.) was sandwiched between both electrodes. During the cell operation, the anode was fed with an aqueous hydrazine solution containing 1 M NaOH. The fuel cell with the prepared ionomer binder performed better than that comprising an electrically inactive poly(vinylidene fluoride) which indicates the enhanced anion transport in the catalyst layer.

Switzer et al. [6] prepared membrane electrode assemblies (MEAs) for an alkaline fuel cell using two types of ionomers: one with a poly(phenylene) backbone with pendant benzyltrimethylammonium groups and another polysulfone with pendant methylenetrimethylammonium groups. Both ionomers had the same ion exchange capacities but the polysulfone-based one swelled less in water. The application of an ionomer material that is less prone to swelling from hydration results in stronger catalyst-ionomer interfacial interactions.

Li et al. [2] added A3-solution or PTFE-emulsion to the catalyst inks. After drying, the A3 ionomer formed a film-like structure,

which resulted in a decrease in the active surface area of the catalysts. The dried PTFE formed a porous structure, which adheres to but not covers the catalyst particles. When a direct ethanol fuel cell was fed with an ethanol solution without added KOH, the best results were obtained with MEAs impregnated with an optimum amount of A3 ionomer. When feeding ethanol-KOH solution, the best performance (in the region of high current density) was achieved with an incorporated PTFE binder.

Similarly, Bunazawa and Yamazaki [7] prepared MEAs using catalyst inks with an added anionic ionomer A3 (Tokuyama). The properties of MEAs were strongly ionomer content dependent. Direct methanol fuel cells showed relatively good performance even when non-alkaline fuel (1M methanol) was used but their performance was extremely enhanced by the addition of NaOH.

Varcoe et al. [8,9] showed that the presence of M^+OH^- in an aqueous methanol fuel is not needed in the operation of alkaline direct methanol fuel cells. They used as an anionic binder poly(vinylbenzyl chloride) dissolved in ethyl acetate, which was sprayed onto the catalyzed sides of electrodes and then immersed in *N,N,N',N'*-tetramethylhexane-1,6-diamine and converted to OH^- form by soaking in aqueous KOH.

Wu and Scott et al. [10,11] tested anionic binders in a “zero-gap” alkaline anion exchange membrane water electrolyser. Deionised water was only supplied into the anode and cathode chambers. The solutions of synthesized anionic ionomers formed together with catalytic particles catalyst inks. The inks were coated onto each side of an anion-exchange membrane. The anionic ionomers were either synthesized by the copolymerization of 2-dimethylaminoethyl methacrylate, 2,2,2-trifluoroethyl methacrylate and butyl methacrylate followed by quaternization with CH_3I , or methylated melamine grafted poly vinyl benzyl chloride. The current density performances of electrolyzers could have been better if KOH solution was employed instead of deionized water but, nevertheless, the electrolyzers performed well.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an attractive material for the preparation of membranes [12–14] because it exhibits excellent film-forming properties, it is chemically and thermally resistant and can be easily derivatized by various polymeranalogical reactions [15]. The bromination of PPO leads under the conditions of free-radical reaction to the bromomethylated PPO, which reacts readily with tertiary amines to yield positively charged quaternary ammonium salts [16,17].

The aim of this work was the preparation of an anionic ionomer based on quaternized PPO soluble in low boiling point solvents and its testing as an electrode binder in an alkaline water electrolyzer.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (powder, Aldrich) (PPO), bromine (ACS reagent, Sigma-Aldrich), chlorobenzene (ACS reagent, Sigma-Aldrich), trimethylamine (TMA) (25 wt% solution in water, Aldrich), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (PENTA), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (PENTA), 60 wt% PTFE (Ion Power), Pt catalyst C2-30 (E-TEK) were used as received.

2.2. Bromination of PPO

Bromine solution in chlorobenzene (20%) was slowly added under stirring to 9% PPO solution in chlorobenzene (132 °C). The reaction mixture was further stirred for 2 h at 132 °C and then it was cooled down to the room temperature. The solution was precipitated into ethanol, the precipitate filtered off, washed with ethanol and dried at 50 °C. The ratio of bromine/PPO (structural unit) see Table 1.

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