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Acid resistant sulphonated poly(vinylidene fluoride-co-hexafluoropropylene)/graphene oxide composite cation exchange for water splitting by iodine-sulfur bunsen process for hydrogen production

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A B S T R A C T
The acid/oxidative-resistant aliphatic-polymer-based cation-exchange membrane (CEM) is urgently required for water splitting by iodine-sulfur electrochemical Bunsen process (I-S cycle). Under operating environment of I-S cycle, commercially available CEM (perfluorosulfonic acid polymers such as Nafion) exhibits excessive mass transfer *via* electro-osmosis and its conductivity deteriorates due to membrane dehydration, while aromatic hydrocarbon based polymers showed short lifetimes due to the oxidative degradation. Herein, we achieved partial sulphonation of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) to introduce hydrophilic character in the polymer matrix, and prepared sulphonated PVDF-co-HFP (SPVDF)/sulphonated GO (SGO) composite acid resistant CEMs with different composition for water splitting via I-S process for hydrogen production. These CEMs were extensively characterized for their morphological characteristics, ion-exchange capacity (IEC), water uptake, conductivity, and stabilities (mechanical, chemical, and thermal) in comparison with state-of-art Nafion117 membrane. About 3-fold high bound water content of suitable assessed SPVDF/SGO40 CEM (bound water content: 3.17%) in compare with Nafion 117 (bound water content: 1.04%) avoids the membrane dehydration and thus any deterioration in membrane conductivity.

Iodine−sulfur (I−S) Bunsen process was successfully performed by membrane electrolysis in a two-compartment electrolytic cell (direct contact-mode) using SPVDF/SGO composite CEMs of different compositions. Theoretical and experimental values of acid produced in the anolyte and catholyte, showed good agreement. Further, relatively high current efficiency (close to 100%) for electrochemical Bunsen process using SPVDF/SGO40 CEM confirmed absence of any side reaction, while approximately 300 kJ mol-H_2^{-1} energy was consumed to produce 1 mol of H_2. In spite of low conductivity in compare with state-of-art Nafion 117 membrane, SPVDF/SGO40 composite CEM was assessed as suitable candidate for water splitting via I-S (Bunsen) process because of its low-cost nature, high bound water content and excellent stabilities in highly acidic environment attributed to the partial fluorinated segments in the membrane matrix.

Keywords: Cation exchange membrane; Water splitting; I-S Bunsen process; Hydrogen production.