

Permethylcobaltocenium Based Hydroxide Exchange Membranes with High Stability

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Hydroxide (OH⁻) exchange membranes (HEMs) are attractive energy conversion electrochemical devices (fuel cells, electrolyzers, and solar hydrogen generators) owing to their intrinsic ability to work with non-precious-metal catalysts as well as CO₂-containing air^[1]. However, unlike proton (H⁺) exchange membranes (PEMs) that are based on the highly stable sulfonic-acid functional group (-SO₃H) and thus have excellent chemical and thermal stability, ammonium-based HEMs have shown limited chemical stability. Alternative cationic functional groups based on the same nitrogen element (such as pyridinium, guanidium, and imidazolium) and other elements (phosphorus: phosphonium, sulfur: sulfonium, and ruthenium: bis(terpyridine)ruthenium complex^[2]) have also been introduced, bringing new features (improved solubility, improved thermal stability, and/or increased charge number) for HEMs but the experimental data suggest much more chemical stability is still desired. The limited chemical stability of ammonium and other cations may be rationalized on the basis of their valence electron structure that allows for many possible degradation pathways.

Alkali metal cations (typically, Li⁺, Na⁺, and K⁺) have excellent chemical stability, because of their non-flexible closed-shell valence electron configurations ([1s²], [2s²2p⁶], [3s²3p⁶], respectively) that are the same as those of noble gases, but they are very challenging to immobilize for HEM applications. Bearing a unit of positive charge, biscyclopentadienyl cobalt sandwich cation (e.g., (C₅H₅)₂Co(III)⁺, or cobaltocenium) satisfies the 18-electron rule for transition metal complexes, in which Co(III) also has closed-shell valence electron configuration. The cobaltocenium hydroxide is considered as a strong base, and in fact the cobaltocenium is the most stable metallocenium in alkaline media^[3]. Equally importantly, cobaltocenium can also be immobilized to polymers in both main-chain and side-chain.

Permethylcobaltocenium, i.e., decamethylated cobaltocenium, is expected to have even higher structure stability than the normal cobaltocenium, due to the charge delocalization caused by strong electron donation from the ten methyl groups^[4]. This is evidenced by over 600 mV negative shift of formal potential observed (-1.24 of (C₅Me₅)₂Co(III)⁺/(C₅Me₅)₂Co(II) vs. -0.63 V of (C₅H₅)₂Co(III)⁺/(C₅H₅)₂Co(II) referring to the SHE, the same solvent of CH₂Cl₂^[5]). Here we present, for the first time, the permethylcobaltocenium-functionalized polymer HEMs that show very high thermal and chemical stability, promising to applications in durable and robust electrochemical devices.

References

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