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Evaluation of a Ag/Ag₂S reference electrode with long-term stability for electrochemistry in ionic

liquids

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Abstract

We report on a reference electrode designed for use in ionic liquids, based on a silver wire coated with silver sulfide. The reference electrode potential is determined by the concentrations of Ag* and S²-, which are established by the solubility of the Ag₂S coating on the Ag wire. While potential shifts of more than 100 millivolts during an experiment have been reported when using silver or platinum wire quasi-reference electrodes, the reference electrode reported here provides a stable potential over several months of experimental use. Additionally, our reference electrode can be prepared and used in a normal air atmosphere, and does not need to be assembled and used in a glovebox, or protected from light. The reference electrode has been characterized by voltammetry measurements of ferrocene and cobaltocenium hexafluorophosphate, and was found to slowly drift to more positive potentials at a rate of < 1 mV/day for five of the six ionic liquids investigated. This slow drift is thought to be caused by the slow uptake of water by the ionic liquids, as the reference electrode was found to have a small sensitivity to water.

Keywords: Reference electrode, room temperature ionic liquid, non-aqueous electrochemistry, silver, quasi-reference electrode.

1. Introduction

Electrochemical measurements in aqueous solutions are typically measured against a well-characterized and widely used reference electrode (RE), such as silver/silver chloride (Ag/AgCl),

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