Supporting Information for:

Low overpotential water oxidation to hydrogen peroxide on manganese dioxide catalysts

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Titration of hydrogen peroxide in BAS-IL ionic liquid

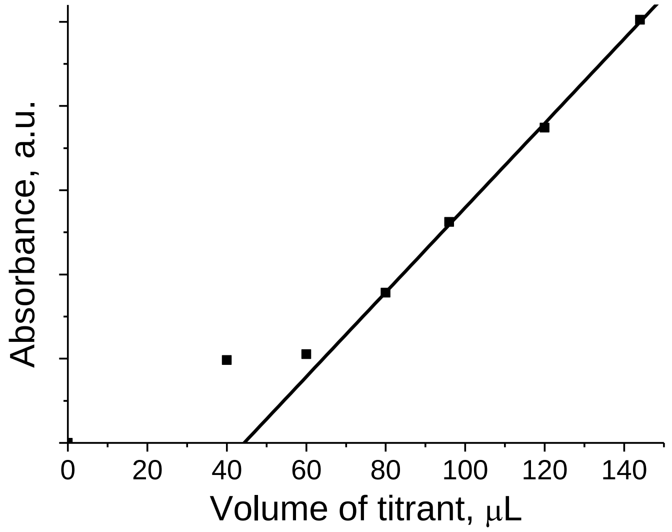

Figure 1. Absorbance of MnO_4^- at 565 nm added to the BAS-IL electrolyte after electrolysis (200mC) to form hydrogen peroxide.

Stability of Electrolyte to oxidation

Stability of the electrolyte was tested using standard hydrogen peroxide as a strong oxidizing agent. In a typical procedure 10^{-3} moles of hydrogen peroxide was added to the 1 ml of as prepared BAS electrolyte at pH10. After about an hour hydrogen peroxide in the electrolyte was slowly disproportionated using MnO_2 powder as catalyst. Nuclear magnetic resonance (NMR) spectroscopy analysis and mass spectroscopic analysis of the electrolyte before and after treatment with hydrogen peroxide is shown below.

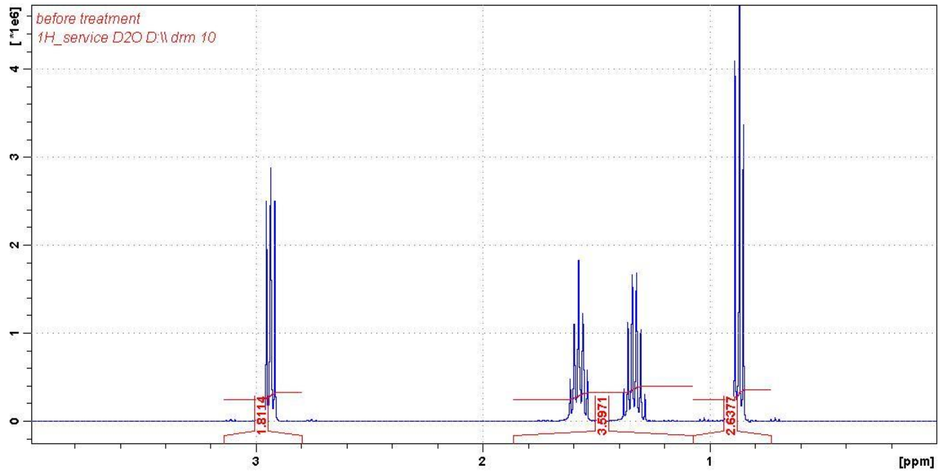

Figure 2. NMR spectrum of the as prepared BAS electrolyte at pH10.

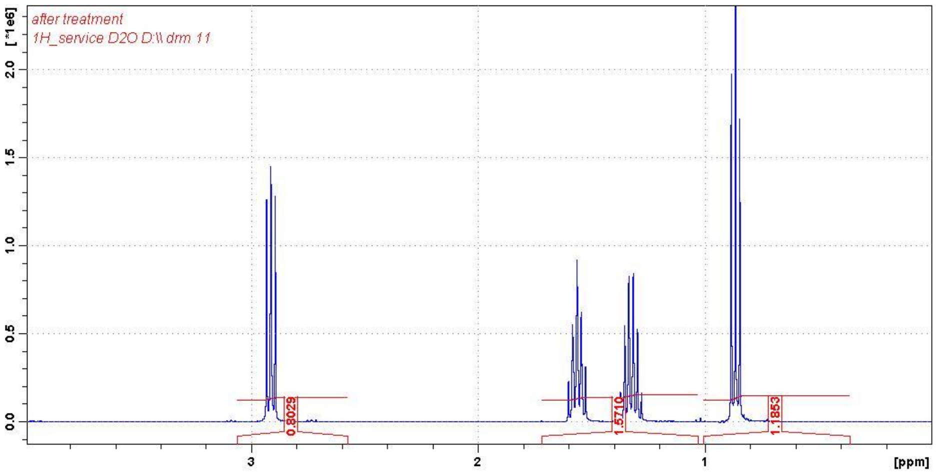

Figure 3. NMR spectrum of the BAS electrolyte at pH10 after treatment with hydrogen peroxide.

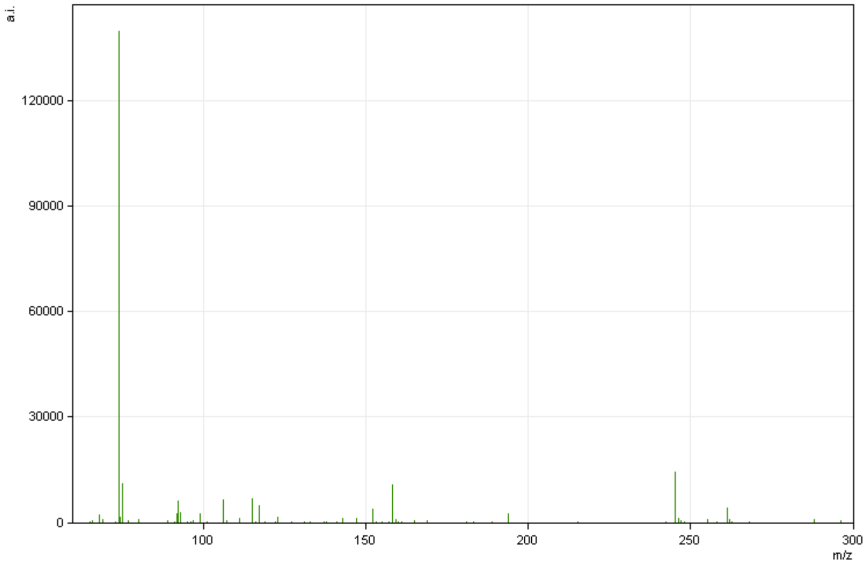

Figure 4. Mass spectrum of the as prepared BAS electrolyte at pH10.

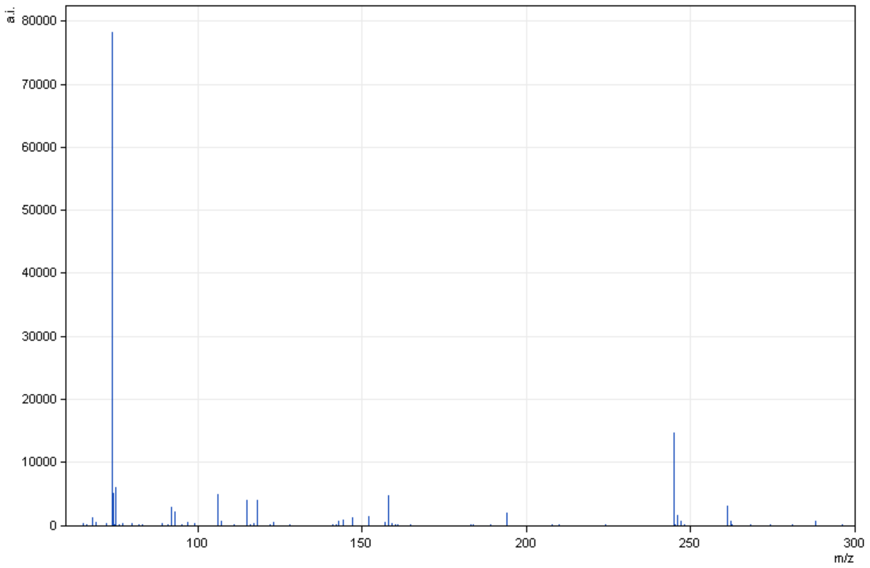

Figure 5. Mass spectrum of the BAS electrolyte at pH10 after treatment with hydrogen peroxide.

Stability of the electrolyte was also tested after prolong electrochemical experiments. In a typical procedure oxidation equivalent to a charge of 1.8 C was passed per 1 ml of as prepared BAS electrolyte at pH10. Then hydrogen peroxide in the electrolyte was slowly disproportionated using MnO_2 powder as catalyst. Nuclear magnetic resonance (NMR) spectroscopy analysis and mass spectroscopic analysis of the electrolyte before and after treatment with hydrogen peroxide is shown below.

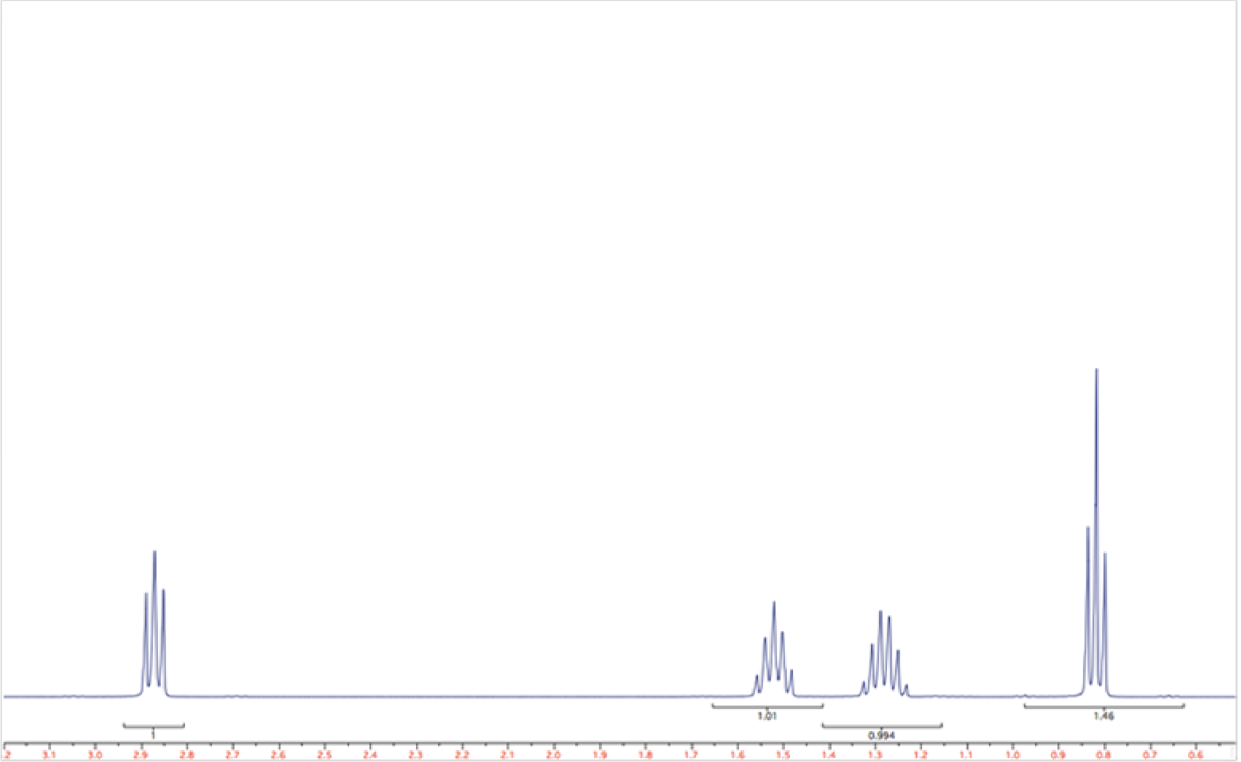

Figure 6. NMR spectrum of the as prepared BAS electrolyte at pH10.

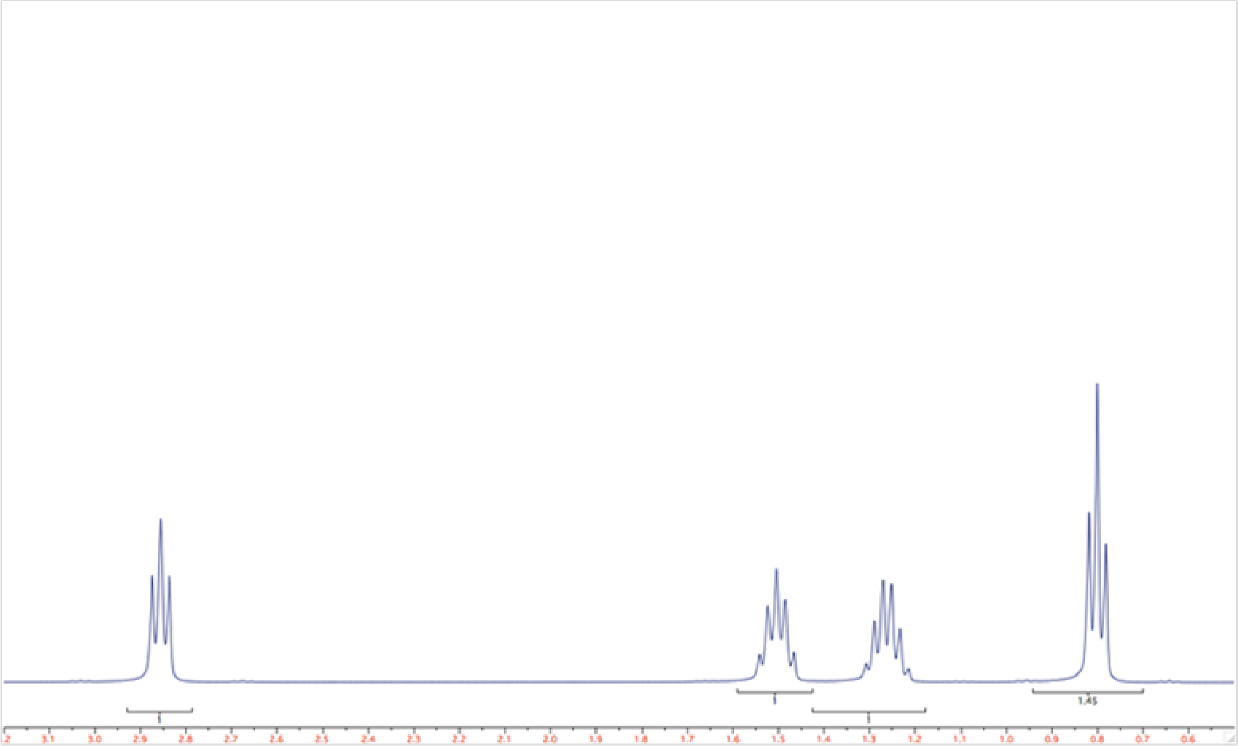

Figure 7. NMR spectrum of the BAS electrolyte at pH10 after electrochemical oxidation.

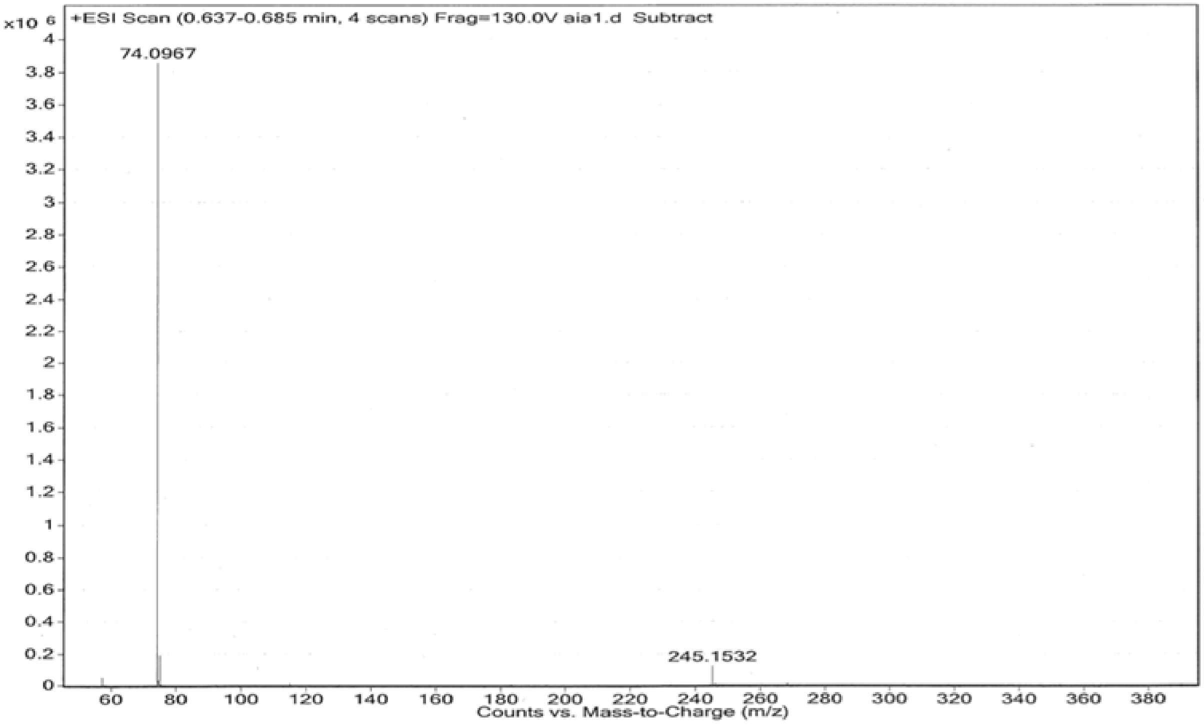

Figure 8. Mass spectrum of the as prepared BAS electrolyte at pH10.

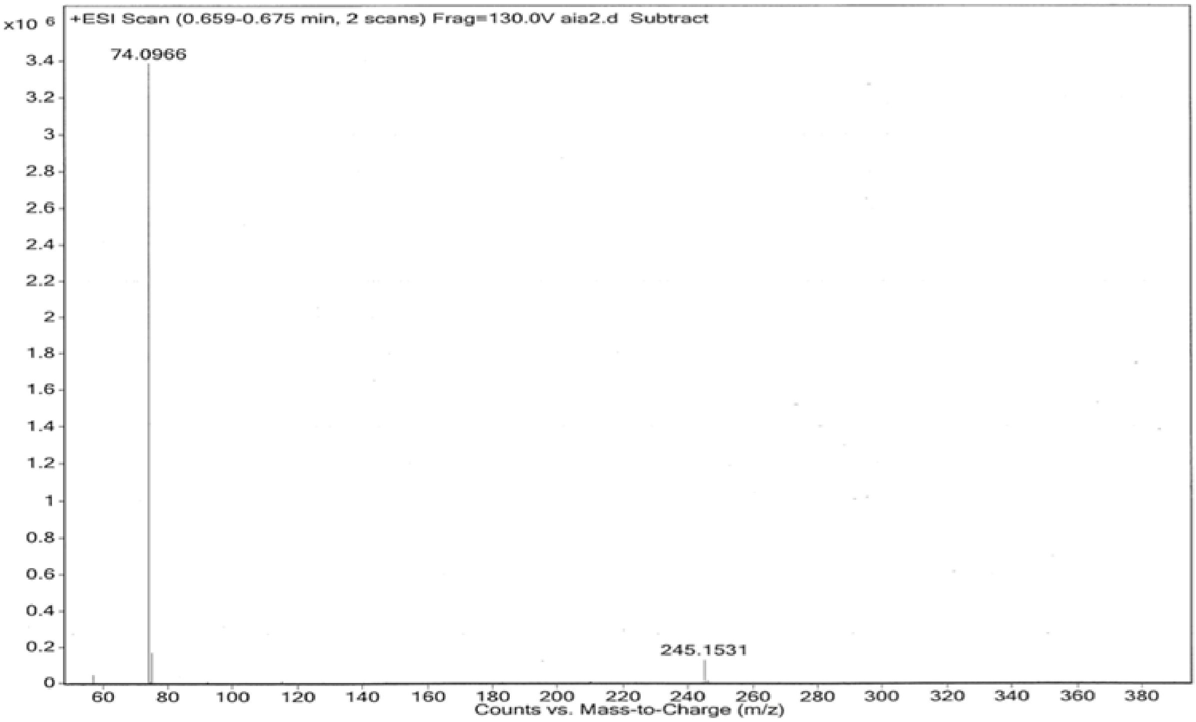

Figure 9. Mass spectrum of the BAS electrolyte at pH10 after treatment with hydrogen peroxide.

Oxygen Generation

The amount of oxygen generated during oxidation using $KMnO_4$ was recorded using a custom built, gas-tight cell with a total volume of 7 ml and filled with 5 ml of electrolyte used for titration, leaving 2 ml of head space volume. A fluorescent sensor probe placed in the head space was used to detect the oxygen concentration. The response from the O_2 sensor, recorded at 1 s intervals, was converted into the partial pressure of O_2 in the headspace using a two-point calibration curve (air, 20.9% O_2; and high purity N_2, 0% O_2). The amount of oxygen in the head space was calculated by converting the measured partial pressure of O_2 into µmols, on the basis of a head space volume of 2 mL. Figure 10 shows response from the oxygen sensor during standard titration, that is equivalent to an 8.66 10^{-7} µmoles of oxygen. Theoretical oxygen in this experiment was 1.4 10^{-6} µmoles. Thus the detected amount of oxygen is about 62% of theoretical. The lower than theoretical is expected given that the H2O2 in this electrolyte undergoes constant disproportionation.