Supplementary Material (ESI) for Chemical Communications

Electrosynthesis of hydrogen peroxide in room temperature ionic liquids and *in situ* epoxidation of alkenes

Michael Chi-Yung Tang[#], Kwok-Yin Wong[#], and Tak Hang Chan[#]

[#]Department of Applied Biology and Chemical Technology and the Open Laboratory for Chirotechnology, Institute of Molecular Technology for Drug Discovery and Synthesis,
The Hong Kong Polytechnic University,
Hung Hom, Hong Kong SAR, China

Supporting Information

Experimental Procedures

All chemicals were purchased from Aldrich and high purity oxygen (>99.7%) was provided by Hong Kong Oxygen Co. The working electrode was reticulated vitreous carbon (RVC) with 60 pores per inch and Nafion® 424 cation permeable membrance were purchased from ERG Materials & Aerospace Cooperation.

Instrumentation

^{1}H and ^{13}C NMR spectral measurements were carried out on a Bruker DPX-400MHz NMR spectrometer. An unmodified household microwave oven (SHARP R342D M/OVEN 34L 1100W T; microwave frequency 2450MHz) was used for the preparation of [bmim][BF$_4$]. EG&G Princeton Applied Research Potntiostat/Galvanostat (Model 273A) was used for batch and continuous flow electrolysis.

Preparation of 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF_4]

[Bmim][Br] and [Bmim][BF_4] were prepared according to a literature procedure using water-moderated microwave process.[1] The [bmim][BF_4] was purified by filtration of silica gel and dried overnight with anhydrous magnesium sulfate.

Hydrogen peroxide generation and determination using the batch electrolysis

Fig 1 shows the electrochemical cell of RVC (25mm x 10mm x 12.5mm) with 60 pores per inch and the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum gauze placed in the anodic compartment, separated by a Nafion® 424 cation permeable membrane. Constant applied potential was applied to the electrochemical cell by potentiostat. The cathodic and anodic compartments had the same volume of [bmim][BF_4] (5 mL) containing the same proportion of water. The catholyte was bubbled with oxygen for 30 minutes to allow sufficient solubilization before the experiments. The oxygen was continuously passed through the catholyte throughout the experiments. During the experiments, both catholyte and anolyte were stirred with magnetic stirrers. The concentration of electrogenerated hydrogen peroxide was determined by differential pulse voltammetry, based on the oxidation of hydrogen peroxide at a platinum electrode. It was continuously carried out after the electrochemical cell had consumed a certain amount of charge. After the experiment, a known volume of catholyte was extracted and a series of known amount of hydrogen peroxide was added. The differential pulse voltammetry was recorded again to produce the calibration curve; and the hydrogen peroxide concentration could be determined by

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[1] Law, M. C.; Wong, K. Y.; Chan, T. H. *Green Chem.* **2002**, *4*, 328-330.

back extrapolation.

Hydrogen peroxide generation and determination using the continuous flow electrolysis with [Bmim][BF$_4$]-water or 0.04M NaOH.

Fig 2 shows the electrochemical micro flow cell (ElectroCell AB, Sweden) of the continuous electrolysis of [Bmim][BF$_4$] with water. The working electrode was a RVC (5mm x 27mm x 33mm) with 60 pores per inch mounted on a solid graphite support. The RVC was glued onto the graphite support by conducting glue made of epoxy adhesive and graphite fine powder. The counter electrode was a platinum plate placed in the anodic compartment, separated by a Nafion® 424 cation permeable membrane. Both compartments were circulated by precision Masterflux pump with constant flow rate connecting with Telfon tubings. The cathodic and anodic compartments had the same volume of [bmim][BF$_4$] (20mL) containing the same proportion of water or 0.04M NaOH (8:2, v/v). Both cathodic and anodic electrolytes were circulated by pump throughout the experiment. The catholyte was continuously bubbled with oxygen. At certain time intervals during electrosynthesis, typically a 0.1ml reaction mixture was withdrawn from the micro flow cell and the hydrogen peroxide content of the reaction mixture was determined by standard titration with $KMnO_4$[2].

Hydrogen peroxide generation and determination for the continuous flow electrolysis in [Bmim][BF$_4$]-Na_2CO_3

Experimental conditions, procedures and electrochemical setup were used which were the same as the continuous flow electrolysis in [Bmim][BF$_4$]-water or 0.04M NaOH. Both cathodic and anodic compartments had [Bmim][BF$_4$] (20 mL) containing 0.05M

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[2] Schumb, W. C. *Hydrogen peroxide*; Reinhold: New York, 1955.

Na_2CO_3 (8:2 v/v). The hydrogen peroxide concentration in [Bmim][BF_4]-Na_2CO_3 was also determined by standard titration with $KMnO_4$. The amount of hydrogen peroxide generated was similar to that with 0.04M NaOH.

Typical procedure for the epoxidation of alkenes with electrogenerated hydrogen peroxide in [bmim[[BF_4]

The alkene (0.35 mmol) was added to [bmim][BF_4]–NaOH mixture (12 mL) with electrogenerated hydrogen peroxide. The reaction mixture was stirred vigorously at room temperature for the time period indicated in Table 2. When the reaction was completed, the mixture was extracted with diethyl ether (5 x 5mL)[3], dried over sodium sulfate and the solvent was removed by rotary evaporator to give the desired product. The desired products were identified by ^1H and ^{13}C NMR. The percentage yields were determined by GC-MS with internal standard.

Recovery and reuse of [bmim][BF_4]

After diethyl ether extraction of the epoxides in the first cycle, the recovered [bmim][BF_4]-NaOH mixture was put under vacuum to remove solvent. The recovered [bmim][BF_4]-NaOH mixture (1 mL) was weighed to obtain the density. The volume ratio of [bmim][BF_4] to NaOH solution in the recovered mixture was determined according to a calibration curve of the density of [bmim][BF_4]-NaOH versus volume ratio of [bmim][BF_4] to NaOH solution. An appropriate amount of water was then added to the recovered [bmim][BF_4]-NaOH mixture to bring the volume ratio back to the optimized 8:2 (v/v). After such compensation of water, the recovered [Bmim][BF_4]-NaOH mixture was then used for the electrogeneration of hydrogen

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[3] It is presumed that the electrohpilic alkenes and epoxide can be extracted by supercritical carbon dioxide in place of diethyl ether. See: Bortolini, O.; Conte, V.; Chiappe, C.; Fantin, G.; Fogagnolo, M.; Maietti, S. *Eur. J. Org. Chem* **2003**, 4804-4809

peroxide in the same manner as before to proceed to the next cycle.

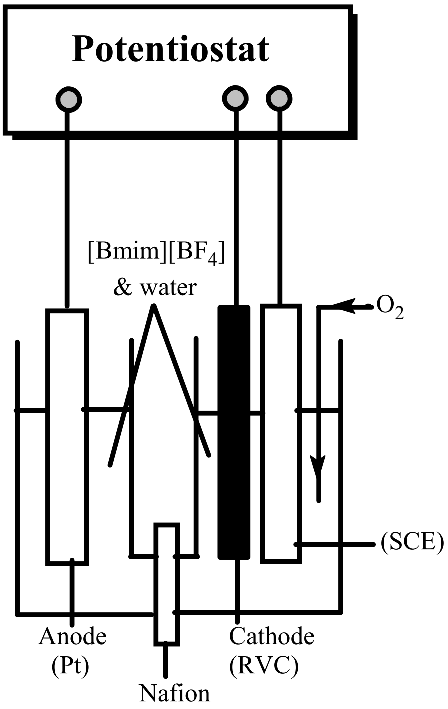

Figure 1. The electrochemical H cell for batch electrolysis of [Bmim][BF_4]-water mixture

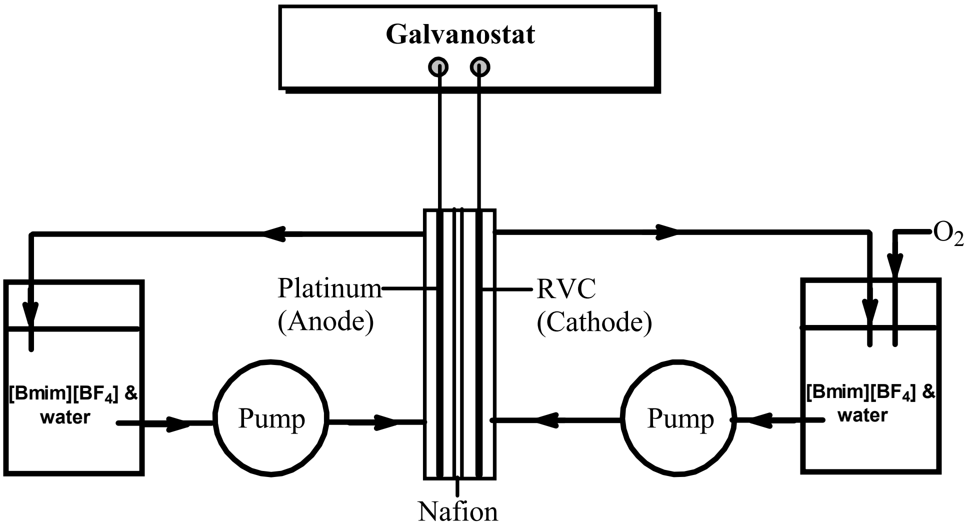

Figure 2. The electrochemical micro flow cell for continuous flow electrolysis of [Bmim][BF_4]-water or NaOH mixture