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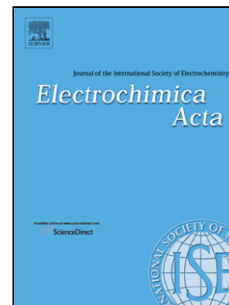
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**The electrochemistry of tetrapropylammonium perruthenate, its role in the oxidation of primary alcohols and its potential for electrochemical recycling**

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**Abstract**

The search for strategies aiming at more sustainable (oxidation) reactions has led to the application of electrochemistry for recycling the spent catalyst. In this work, an electrochemical study of the tetrapropylammonium perruthenate catalyst (TPAP) and its activity towards a primary alcohol, *n*-butanol, has been carried out as well as a control study with *tert*-butanol. The redox chemistry of TPAP and the transition between the perruthenate anion and ruthenium tetroxide in a non-aqueous solvent have been, for the first time, investigated in depth. The oxidation reaction of *n*-butanol in the presence of TPAP has been electrochemically elucidated by performing potentiostatic experiments and registration of the corresponding oxidation current. Furthermore, it was shown that, by applying a specific potential, the reoxidized TPAP is able to oxidize/convert the primary alcohol, paving the way for practical applications using TPAP in electrochemical synthesis. The conversion of *n*-butanol into *n*-butanal was proven by the use of GC-MS.

**Keywords:** tetrapropylammonium perruthenate; acetonitrile; electrochemical recycling; alcohol oxidation; electrosynthesis

## 1. Introduction

The main current application of the perruthenate anion is situated in the field of organic chemistry where it is used for the selective conversion of alcohols into aldehydes. The synthesis of the tetrapropylammonium salt of the anion (tetrapropylammonium perruthenate; TPAP) by Ley and coworkers made it soluble in organic solvents and available for oxidation reactions [1]. It did become a popular reagent as it combines some desirable properties, namely air stability, commercial availability, performance at room temperature and high chemoselectivity. As ruthenium is a rather expensive transition metal and in the strive towards more sustainability, catalytic oxidation methods have been developed using catalytic amounts of TPAP in combination with *N*-methylmorpholine *N*-oxide (NMO) as a stoichiometric oxidant [2]. Commonly, dichloromethane or acetonitrile or a combination of these two solvents is used with the addition of powdered 4 Å molecular sieves to remove water formed during the reaction. Recent advances with the TPAP/NMO method has made the oxidation of primary alcohols to carboxylic acids possible [3]. Here 10 equivalents of NMO are added, the excess of NMO stabilizes the formation of an aldehyde hydrate, which is a necessary step in the controlled oxidation of aldehydes to carboxylic acids. Within the same search for more environmentally friendly methods, it has been found that oxygen as well can be used as a stoichiometric oxidant to oxidize alcohols in combination with catalytic amounts of TPAP [4,5]. Furthermore, it has been shown that TPAP can be used as a heterogeneous catalyst with NMO or oxygen as a stoichiometric oxidant. Most of the suggested approaches consist of an ionic bond between the perruthenate anion and a heterogeneous quaternary ammonium cation, for example the polystyrene supported perruthenate [6], the mesoporous silicate MCM-41 with immobilized perruthenate [7] or the

alkyl-imidazolium-based periodic mesoporous organosilica with supported perruthenate [8]. Finally, a sol-gel encapsulated TPAP [9] strategy is also reported.

Despite the fact that the perruthenate anion is an important catalyst in organic synthesis, its electrochemical behavior in organic solvents has never been studied before. A study of the catalyst in joint reaction with the oxidation of alcohols might be interesting to see if strategies can be found to make electrochemical recycling of the oxidant possible. Organic electrosynthesis [10] agrees well with the principles of green chemistry [11] as it is possible to regenerate the catalyst at the electrode surface at a fixed potential. Therefore, no stoichiometric co-oxidant has to be added. As a result a stream of toxic waste is avoided and a more sustainable oxidation becomes possible.

The perruthenate anion ( $\text{RuO}_4^-$ ) is the active part of TPAP and the formal oxidation state of ruthenium in the perruthenate anion is +7 ( $\text{Ru}^{\text{VII}}$ ). This anion has already been studied electrochemically in water but without taking into account the presence of alcohols [12]. In this study, different ruthenium-oxy species were observed: ruthenium tetroxide ( $\text{RuO}_4$ ), the ruthenate anion ( $\text{RuO}_4^{2-}$ ) and ruthenium oxide ( $\text{RuO}_2$ ), with an oxidation state of respectively +8 ( $\text{Ru}^{\text{VIII}}$ ), +6 ( $\text{Ru}^{\text{VI}}$ ) and +4 ( $\text{Ru}^{\text{IV}}$ ). A few methods have already been developed, making use of the electrochemical recycling of ruthenium-oxy species for the catalytic oxidation of alcohols, but all focusing on  $\text{RuO}_2$ . Therefore water has to be added as a solvent or co-solvent. For example,  $\text{RuO}_4$  can function as the oxidant in a two phase system of tetrachloromethane and water [13]. In this case, active chloride species ( $\text{Cl}_2$  or  $\text{Cl}^+$ ) are generated at the electrode surface in the sodium chloride solution (water phase) and oxidize  $\text{RuO}_2$  to  $\text{RuO}_4$ , which is responsible for the subsequent oxidation of the alcohol in the organic phase. As this approach still uses another reagent (chloride) as secondary oxidant, this

method cannot be regarded as a pure electrochemical oxidation of the ruthenium catalyst. Moreover it is performed in a toxic solvent, which is considered as an ozone depleting agent [14]. The same author reports on a method in which  $\text{RuO}_2$  is directly oxidized at the electrode surface to a  $\text{Ru}^{7+}$  species in an alkaline acetonitrile/water mixture, followed by the  $\text{Ru}^{7+}$  promoted oxidation of alcohols [15]. This method is presented without any electrochemical investigation. An improved method making use of the neutral conditions of the Ley oxidation would be beneficial. Another strategy that has been used is to make use of  $\text{RuO}_2$  as an electrode material. In basic media the  $\text{RuO}_2$  can be electrochemically oxidized to  $\text{RuO}_4^{2-}$  and  $\text{RuO}_4^-$  which can react with alcohols [16]. Studies have been performed on the oxidation of glucose [17,18] and benzylalcohol [19]. Also, the use of  $\text{RuO}_2$  as a material for pseudocapacitance is currently under examination and it is possible that the formation of the perruthenate anion has an influence on the mechanism explaining the high capacitance of hydrous ruthenium oxide [16].

In this article, the results of an in-depth investigation of the electrochemical behavior of the perruthenate anion in a non-aqueous neutral solvent are presented. Additionally, the oxidation reaction of *n*-butanol in the presence of TPAP has been electrochemically elucidated by performing potentiostatic experiments and by recycling of the spent catalyst under mild conditions.

## 2. Experimental

Anhydrous acetonitrile was purchased from VWR and kept dry over activated molecular sieves under argon atmosphere. Tetrapropylammonium perruthenate (97%) and tetrabutylammonium tetrafluoroborate (for electrochemical analysis, >99.0%) were

purchased from Sigma-Aldrich and used as received. *n*-Butanol was purchased from Merck and used as received.

All electrochemical measurements were performed by using a Potentiostat/Galvanostat PGSTAT 101 from Metrohm, connected with a PC provided with NOVA 1.10 software. A three-electrode cell was used with a platinum working electrode of 2 mm diameter (Metrohm, the Netherlands) or a glassy carbon working electrode of 3 mm diameter, a platinum sheet counter electrode and a bridged Ag/AgCl reference electrode with 2 M LiCl ethanol solution as inner solution and acetonitrile as bridge solution. All potentials mentioned are relative to this reference electrode unless stated otherwise. This reference electrode has a voltage difference of +150 mV versus a standard hydrogen electrode (SHE) and the voltage difference versus the ferrocene redox couple ( $\text{Fc}^+/\text{Fc}$ ) is -500 mV. The working electrode was pretreated by mechanical polishing. It was subjected to sequential polishing with a cloth covered with alumina powder of 1 and 0.05  $\mu\text{m}$  particle size (SPI supplies, USA) for 10 minutes to remove any adherent  $\text{Al}_2\text{O}_3$  particles. The electrode surface was rinsed thoroughly with deionized water and cleaned in an ultrasonic bath containing deionized water for 2 minutes. Next the electrode was rinsed with acetone and dried. Solutions of 0.1 M  $\text{Bu}_4\text{NBF}_4$  in acetonitrile were freshly made and purged with nitrogen gas for 10 minutes to remove oxygen before each measurement. Rotating disk measurements were measured with a controlled speed rotator (Metrohm, the Netherlands). A typical potentiostatic experiment was done as follows, a cell was filled with a freshly prepared solution of 0.1 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_3\text{CN}$  (20 mL), electrodes were added and nitrogen gas was purged for 10 minutes. Then, a constant potential was applied and after 200 seconds TPAP (14 mg, 0.04 mmol) was added, after 300 seconds the rotation was initiated (2000 rpm) and finally after 350 seconds *n*-butanol (37  $\mu\text{L}$ , 0.4 mmol) was added. Electrolysis experiments



were performed in a homemade airtight electrolysis cell. The working electrode used is a reticulated vitreous carbon (RVC) electrode with a surface area of  $10.5 \text{ cm}^2/\text{cm}^3$ . A typical electrolysis experiment was done as follows, the cell was filled with a freshly prepared solution of 0.1 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_3\text{CN}$  (30 mL), electrodes were added and nitrogen gas was purged for 10 minutes. Next TPAP (21 mg, 0.06 mmol) and *n*-butanol (55  $\mu\text{L}$ , 0.6 mmol) were added and a constant potential (or no potential) was applied under stirring for 5 hours at room temperature. The resulting mixture was distilled and samples were taken from the distillate for analysis with gas chromatography–mass spectrometry (GC-MS).

GC-MS samples were analyzed on an Agilent 7890A gas chromatograph connected via splitter to both a quadropole MS and a FID detector. The instrument was equipped with a fused silica capillary column (OPTIMA 5MS Accent – 0.25  $\mu\text{M}$ , 30 m, 0.25 mm ID – manufactured by Machery-Nagel). The column had a silarylene stationary phase with ultra-low bleeding and a polarity similar to 5 % diphenyl/95 % dimethylpolysiloxane (i.e. non-polar) and a maximum temperature of 340°C (isothermal).

### 3. Results and discussion

#### 3.1 Electrochemical screening of TPAP

An electrochemical study of TPAP in a non-aqueous solvent has been performed by using cyclic voltammetry. The use of both dichloromethane and acetonitrile were tested because these are the solvents used for a classical TPAP/NMO oxidation. Dichloromethane was found not to be useful to perform cyclic voltammetry on TPAP as no reproducible redox reactions could be obtained. The redox processes observed are not stable as a function of scan number as can be seen in the supporting information (Figure S1). On the other hand, the use

of acetonitrile was successful and reproducible peaks could be obtained. The metal coordinating properties of acetonitrile could probably account for this different behavior [20]. Other advantages of acetonitrile are its higher conductivity and higher boiling point, so less evaporation occurs under a nitrogen flow. Figure 1 represents the current-potential behavior of 1 mM TPAP in acetonitrile with 0.1 M  $\text{Bu}_4\text{NBF}_4$  as electrolyte and with a scan rate of  $100 \text{ mVs}^{-1}$ . A scan of the platinum electrode in a solution of acetonitrile without TPAP is also shown and in this case no redox processes are observed. In the presence of TPAP four different redox processes can be distinguished. At ca. 0.9 V a first anodic peak  $I_a$  can be observed, upon reversal of the scan direction a cathodic peak  $I_c$  appears around 0.85 V. Towards more negative potentials a new cathodic process  $II_c$  is observed around -1.0 V and upon reversal an anodic wave  $II_a$  is detected around -0.5 V.

In order to investigate the nature and the reversibility of the redox couple I, the dependency of the peak currents of  $I_a$  and  $I_c$  on the scan rate is investigated (Figure 2).

A linear relationship was found between the peak current ( $I_p$ ) and the square root of the scan rate ( $v$ ). A slope of circa 0.5 was found between  $\log I_p$  and  $\log v$ , the inset of Figure 2 represents this relationship for  $I_a$ , following the Randles–Sevcik formula. Additionally, it was observed that the peak potential ( $E_p$ ) remains constant for different scan rates. These results correspond to a reversible diffusion controlled reaction of TPAP [21]. To calculate the number of electrons taking part in the redox process, the difference between  $E_p$  and the half-peak potential ( $E_{p,1/2}$ ) was calculated, theoretically this value should be 56.5 mV divided by the amount of electrons involved [21]. A calculated value of 59.2 mV indicates a reversible

one-electron process. Therefore, it is clear that the reversible peaks of process I are caused by the transition between  $\text{RuO}_4^-$  and  $\text{RuO}_4$  (Scheme 1).

The value for  $E_{p,1/2}$ , i.e. 0.85 V, agrees well with the potential obtained by Lam et al. for the same redox couple in a NaOH solution [12]. To determine the diffusion coefficient of the perruthenate anion, cyclic voltammetry experiments using a rotating disk were performed (Figure 3).

A linear relationship between the square root of the rotation speed ( $\omega$ ) and the limiting current ( $I_l$ ) is observed, confirming that the  $\text{Ru}^{\text{VII}}/\text{Ru}^{\text{VIII}}$  transition is mass-transfer controlled. To the best of our knowledge, for the first time the diffusion coefficient of the perruthenate anion could be experimentally obtained by using the Levich equation [21], giving a calculated diffusion coefficient  $D = 1.72 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

When focusing on  $\text{II}_c$  (see Figure 1) the reduction of the perruthenate anion is examined. No reversible peaks are detected but instead a broad reduction process is observed. Most likely the reduction of  $\text{RuO}_4^-$  to  $\text{RuO}_2$  is occurring here.  $\text{RuO}_2$  is not soluble in acetonitrile and, during our experiments, a layer was deposited on the electrode surface, especially when multiple scans were taken or when a rotating disk electrode was used. Similar observations were made by using glassy carbon electrodes. To identify the product formed, the deposits on the electrode surface were further electrochemically investigated by entrapping the deposit in a thin nafion film. The modified electrode was scanned in a 0.5 M NaOH solution and a similar redox behavior was observed as for commercial  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  (with protective

nafion film) deposited on an electrode surface. Additionally, the modified electrodes (both with unknown deposit and with commercial  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  as deposit) were also tested in a 0.5 M  $\text{H}_2\text{SO}_4$  solution, here a broad peak around 0.4 V versus standard calomel electrode was detected unraveling the redox chemistry of  $\text{RuO}_2$  [16]. These results indicate the formation of ruthenium oxide or a mixture with hydrous ruthenium oxides during the potential cycling in TPAP. It is clear that the presence of  $\text{Ru}^{6+}$  and  $\text{Ru}^{5+}$  could not be electrochemically identified. All CVs indicating the formation of  $\text{RuO}_2$  can be found in the supporting information (Figure S2 + S3).

### 3.2 Alcohol oxidation by TPAP

Initially cyclic voltammetry was used to observe the effect of adding *n*-butanol to a TPAP solution. Not unexpectedly, when doing multiple scans, the formation of a solid on the electrode hampered the analysis. The mechanism of the stoichiometric reaction between TPAP and alcohol (no electrolysis) has been studied before in organic solvents [22,23] and inspired by these investigations we propose the following mechanism:



The perruthenate anion is a two-electron oxidant and oxidizes *n*-butanol to *n*-butanal. The reduction proceeds in multiple steps and the final reduced ruthenium species is  $\text{RuO}_2$ . The formation of  $\text{RuO}_2$  indeed was confirmed by UV-VIS (vide infra). To investigate this mechanism and to see what are the possibilities for recycling the perruthenate ions or other

catalytic ruthenium species during the oxidation of the alcohol, potentiostatic experiments were performed. These experiments were done with a platinum rotating disk electrode under constant potential to record the current as a function of time (Figure 4). The potential applied can have an effect on the different ruthenium intermediates mentioned in the mechanism above. The potential was set at 0.7 V, because the formation of RuO<sub>4</sub> does not yet occur at this potential as can be seen from the cyclic voltammetry scans (Figure 1). In the case when only *n*-butanol is added to the electrolyte solution (Figure 4, curve a), no direct oxidation is expected and indeed no faradaic oxidation current can be observed. When only TPAP is added to the electrolyte solution (Figure 4, curve b), a similar phenomenon occurs, and almost no faradaic oxidation current can be witnessed. When both TPAP and *n*-butanol are added (Figure 4, curve c), a steep rise of the current is detected. In this experiment the reagents are added step by step, first TPAP is added after 150 seconds and in a next step, after 370 seconds, *n*-butanol is added resulting in an increase of the current. This rise of the current is clear evidence that now reoxidation of the spent TPAP is occurring. Unfortunately the exact nature of the species generated at the electrode surface cannot be determined within this set of experiments. As a control experiment *tert*-butanol was added to a TPAP solution under potentiostatic conditions following the same procedure (Figure 4, curve d). *Tert*-butanol cannot be oxidized by TPAP and so no reoxidation of spent TPAP is expected at the electrode surface. Although *tert*-butanol cannot be oxidized by TPAP, the formation of a complex where *tert*-butanol acts as a ligand is possible. From Figure 4 it is clear that indeed no rise of the current is observed. This observation rules out that the current rise is caused by the oxidation of this complex. It is also observed from Figure 4 that the oxidation current drops after ca 300 seconds. The reason for this is unclear at the moment but the formation of a deposit on the electrode (such as RuO<sub>2</sub>) and the formation of inert catalyst species

might be the cause. The formation of  $\text{RuO}_2$  in solution could be confirmed by UV-VIS measurements (see supporting information) after the potentiostatic experiment. When using a glassy carbon working electrode similar results as in Figure 4 could be observed. No different behavior could be seen when varying the electrode material.

Next the influence of applying higher potentials on the oxidation current is examined by following the same stepwise procedure. At potentials higher than 0.8 V, the perruthenate anion is oxidized at the electrode surface with formation of ruthenium tetroxide. In Figure 5 the potentiostatic response of TPAP at 1.1 V and the addition of *n*-butanol are shown. In this experiment TPAP was added after 180 seconds (Figure 5, a), then rotation was initiated at 300 seconds (Figure 5, b). The current increase observed is caused by the oxidation of the perruthenate anion to ruthenium tetroxide. Around 330 seconds, *n*-butanol is added to the solution (Figure 5, c), followed by a drop of the current which is caused by the reaction of perruthenate with *n*-butanol in the bulk solution. Although the  $\text{RuO}_4$ , produced in the previous step, is also able to oxidize *n*-butanol [20], its influence is negligible because of the very low concentration compared to the bulk concentration of perruthenate. The concentration of the perruthenate at the electrode surface is decreasing as it is consumed by the alcohol. This is followed by a new rise of the current, caused by reoxidation of the spent TPAP. The current is then at a similar level as with a potential of 0.7 V. This indicates that a higher potential does not have a large influence on the reoxidation of the spent TPAP.

To get an overview of the potentiostatic response at different potentials, experiments were performed over a broad potential range. In Figure 6 the potentiostatic response for TPAP

and *n*-butanol is shown at different potentials. The time of *n*-butanol addition is set at 0 s. Consequently, at 0 s, 2 mM TPAP, 20 mM *n*-butanol and 0.1 M electrolyte are present in the acetonitrile solution (under constant rotation).

When applying a potential below 0.8 V, it is clear that initially no oxidation current is observed at 0 s as no oxidation reaction of TPAP might occur (see Figure 4). A small rise of the current can be observed after ca 60 s when a potential of 0.0 V is applied. When raising the potential from 0.3 to 0.5 and 0.7 V, a gradual rise in the current height can be detected. When looking at higher potentials than 0.8 V, an oxidation current ( $\text{Ru}^{\text{VII}}$  to  $\text{Ru}^{\text{VIII}}$ ) is present from the start onwards. Due to *n*-butanol oxidation with TPAP, a decrease of the current is detected until a steady state situation is reached. The value for this steady state current is similar to the value obtained in the 0.7 V experiment. It can be concluded that a potential of 0.7 V is sufficient to reoxidize the spent TPAP. No significant influence of oxidation to  $\text{Ru}^{\text{VIII}}$  at higher potentials is observed.

For the oxidation of *n*-butanol on a larger scale, an airtight homemade electrolysis cell was used with a reticulated vitreous carbon (RVC) working electrode, which has a high surface area. The cell was placed under an inert nitrogen atmosphere to exclude the interference of atmospheric oxygen. A constant potential was applied of 0.7 V or 1.3 V to a solution of *n*-butanol and TPAP in electrolyte solution for 5 hours. Next, the resulting mixture was distilled to obtain a solution of the volatile reaction products and remaining starting alcohol in acetonitrile. This distillate was analyzed by means of GC-MS and separated peaks of *n*-butanol and *n*-butanal were detected. In case no potential was applied a 5/95 ratio of butanal/butanol was observed, while at 1.3 V this ratio changed in favour of butanal (34/66 :

butanal/butanol). Obviously, when no potential is applied, only the stoichiometric oxidation of *n*-butanol can take place, using the 0.1 equivalents of TPAP present and giving rise to a maximum of 10% conversion of *n*-butanol (Figure 7).

The highest conversion of *n*-butanol into *n*-butanal was obtained by applying a potential of 1.3 V, indicating that on a larger scale the electrosynthesis benefits from these higher oxidation potential values. At this higher potential the conversion of *n*-butanol increased from 5 % to 34%, which shows that reoxidation of the spent TPAP is possible and is able to further oxidize the alcohol.

#### 4. Conclusions

An electrochemical in-depth study of the TPAP catalyst in an organic solvent has been carried out. A diffusion coefficient was calculated for the perruthenate anion using the Levich equation, giving a value of  $D = 1.72 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . Via potentiostatic experiments the interaction between TPAP and a primary alcohol, *n*-butanol, was elucidated. Interestingly, an oxidation current has been observed, indicating the conversion of the alcohol in interaction with the catalyst. The oxidation current reflects the reoxidation of spent TPAP inducing the conversion of the alcohol. By using GC-MS, it has been shown that *n*-butanol can be oxidized into *n*-butanal via the reoxidation of spent TPAP.



## References

- [1] W.P. Griffith, S.V. Ley, G.P. Whitcombe, A.D. White, Preparation and use of tetra-n-butylammonium per-ruthenate (TBAP reagent) and tetra-n-propylammonium per-ruthenate (TPAP reagent) as new catalytic oxidants for alcohols, *J. Chem. Soc., Chem. Commun.* (1987) 1625-1627.
- [2] S.V. Ley, J. Norman, W.P. Griffith, S.P. Marsden, Tetrapropylammonium perruthenate,  $\text{Pr}_4\text{N}^+\text{RuO}_4^-$ , TPAP: a catalytic oxidant for organic synthesis, *Synthesis*. (1994) 639-666.
- [3] A.C. Schmidt, C.B. Stark, TPAP-catalyzed direct oxidation of primary alcohols to carboxylic acids through stabilized aldehyde hydrates, *Org. Lett.* 13 (2011) 4164-4167.
- [4] R. Lenz, S.V. Ley, Tetra-n-propylammonium perruthenate (TPAP)-catalysed oxidations of alcohols using molecular oxygen as a co-oxidant, *J. Chem. Soc., Perkin Trans. 1.* (1997) 3291-3292.
- [5] I.E. Markó, P.R. Giles, M. Tsukazaki, I. Chellé-Regnaut, C.J. Urch, S.M. Brown, Efficient, aerobic, ruthenium-catalyzed oxidation of alcohols into aldehydes and ketones, *J. Am. Chem. Soc.* 119 (1997) 12661-12662.
- [6] B. Hinzen, S.V. Ley, Polymer supported perruthenate (PSP): a new oxidant for clean organic synthesis, *J. Chem. Soc., Perkin Trans. 1.* (1997) 1907-1908.
- [7] A. Bleloch, B.F. Johnson, S.V. Ley, A.J. Price, D.S. Shephard, A.W. Thomas, Modified mesoporous silicate MCM-41 materials: immobilised perruthenate-a new highly active heterogeneous oxidation catalyst for clean organic synthesis using molecular oxygen, *Chem. Commun.* (1999) 1907-1908.
- [8] B. Karimi, D. Elhamifar, O. Yari, M. Khorasani, H. Vali, J.H. Clark, et al., Synthesis and characterization of alkyl-imidazolium-based periodic mesoporous organosilicas: a versatile host for the immobilization of perruthenate ( $\text{RuO}_4^-$ ) in the aerobic oxidation of alcohols, *Chem. - Eur. J.* 18 (2012) 13520-13530.
- [9] R. Ciriminna, M. Pagliaro, Tailoring the catalytic performance of sol-gel-encapsulated tetra-n-propylammonium perruthenate (TPAP) in aerobic oxidation of alcohols, *Chem. - Eur. J.* 9 (2003) 5067-5073.
- [10] C. Moinet, J. Hurvois, A. Jutand, Organic and metal-catalysed electrosynthesis, *Adv. Org. Synth.* 1 (2005) 403-453.
- [11] H.J. Schäfer, Contributions of organic electrosynthesis to green chemistry, *C. R. Chimie.* 14 (2011) 745-765.

- [12] K.W. Lam, K.E. Johnson, D.G. Lee, Studies of ruthenium-oxy Species in basic solutions by cyclic voltammetry, *J. Electrochem. Soc.* 125 (1978) 1069-1076.
- [13] S. Torii, T. Inokuchi, T. Sugiura, Indirect electrooxidation of alcohols and aldehydes by using a double mediatory system consisting of ruthenium tetroxide/ruthenium dioxide and chlorine cation/chlorine anion redoxes in an aqueous-organic two-phase system, *J. Org. Chem.* 51 (1986) 155-161.
- [14] R.K. Henderson, C. Jimenez-Gonzalez, D.J.C. Constable, S.R. Alston, G.G.A. Inglis, G. Fisher, et al., Expanding GSK's solvent selection guide - embedding sustainability into solvent selection starting at medicinal chemistry, *Green Chem.* 13 (2011) 854-862.
- [15] S. Torii, A. Yoshida, A novel Ru(VII)/Ru(IV) mediatory system for electrooxidation of primary and secondary alcohols, leading to aldehydes and ketones, *Chem. Lett.* 24 (1995) 369-370.
- [16] C. Lee, A.M. Bond, Revelation of multiple underlying RuO<sub>2</sub> redox processes associated with pseudocapacitance and electrocatalysis, *Langmuir.* 26 (2010) 16155-16162.
- [17] M.E. Lyons, C.A. Fitzgerald, M.R. Smyth, Glucose oxidation at ruthenium dioxide based electrodes, *Analyst.* 119 (1994) 855-861.
- [18] V. Dharuman, K.C. Pillai, RuO<sub>2</sub> electrode surface effects in electrocatalytic oxidation of glucose, *J. Solid State Electr.* 10 (2006) 967-979.
- [19] S.M. Lin, T.C. Wen, Electrocatalytic oxidation of benzyl alcohol in alkaline medium on RuO<sub>2</sub>-coated titanium electrode, *J. Appl. Electrochem.* 25 (1995) 73-79.
- [20] P.H. Carlsen, T. Katsuki, V.S. Martin, K.B. Sharpless, A greatly improved procedure for ruthenium tetroxide catalyzed oxidations of organic compounds, *J. Org. Chem.* 46 (1981) 3936-3938.
- [21] A.J. Bard, L.R. Faulkner, *Electrochemical methods: fundamentals and applications*, 2nd edition, Wiley, 2001.
- [22] M. Hasan, M. Musawir, P.N. Davey, I.V. Kozhevnikov, Oxidation of primary alcohols to aldehydes with oxygen catalysed by tetra-n-propylammonium perruthenate, *J. Mol. Catal. A: Chem.* 180 (2002) 77-84.
- [23] W.D. Chandler, Z. Wang, D.G. Lee, Kinetics and mechanism of the oxidation of alcohols by tetrapropylammonium perruthenate, *Can. J. Chem.* 83 (2005) 1212-1221.

**Figure Captions**

**Scheme 1.** Redox transition between perruthenate and ruthenium tetroxide.

**Figure 1.** Cyclic voltammograms obtained at a Pt electrode in a 0.1 M  $\text{Bu}_4\text{NBF}_4$  acetonitrile solution (a) containing 1 mM TPAP (scans 2 and 5) (b) with a scan rate of  $100 \text{ mVs}^{-1}$ .

**Figure 2.** Cyclic voltammograms of 1 mM TPAP in 0.1 M  $\text{Bu}_4\text{NBF}_4$  acetonitrile solution at a Pt electrode with different scan rates: 50; 75; 100; 150; 250 and  $500 \text{ mVs}^{-1}$ . Inset:  $\log I_p$  versus  $\log v$ .

**Figure 3.** Cyclic voltammograms of 0.5 mM TPAP in a 0.1 M  $\text{Bu}_4\text{NBF}_4$  acetonitrile solution at a Pt electrode with different rotation speeds: 0 (a); 500 (b); 1000 (c); 1500 (d); 2000 (e); 2500 (f) and 3000 (g) rpm. Inset:  $I_l$  versus  $(\omega)^{1/2}$ .

**Figure 4.** Oxidation current response of different species under potentiostatic conditions at 0.7 V with rotating disk Pt electrode (2000 rpm), 20 mM *n*-butanol in an electrolyte solution (a); 2 mM TPAP in an electrolyte solution (b); 20 mM *n*-butanol + 2 mM TPAP in an electrolyte solution (c) and 20 mM *tert*-butanol + 2 mM TPAP in an electrolyte solution (d).

**Figure 5.** Oxidation current response at 1.1 V under potentiostatic conditions with rotating disk Pt electrode: after 180 s 2 mM TPAP is added to the electrolyte/acetonitrile solution (a), rotation (2000 rpm) is initiated after 300 s (b) and 20 mM *n*-butanol is added (c).

**Figure 6.** Oxidation current response at different potentials for 2 mM TPAP + 20 mM *n*-butanol added at 0 s in an electrolyte solution with rotating disk Pt electrode at 2000 rpm.

**Figure 7.** GC-MS of the distillate obtained after electrolysis of a 0.1 M  $\text{Bu}_4\text{NBF}_4$  acetonitrile solution with 2 mM TPAP and 20 mM of *n*-butanol under nitrogen atmosphere.

## Figures

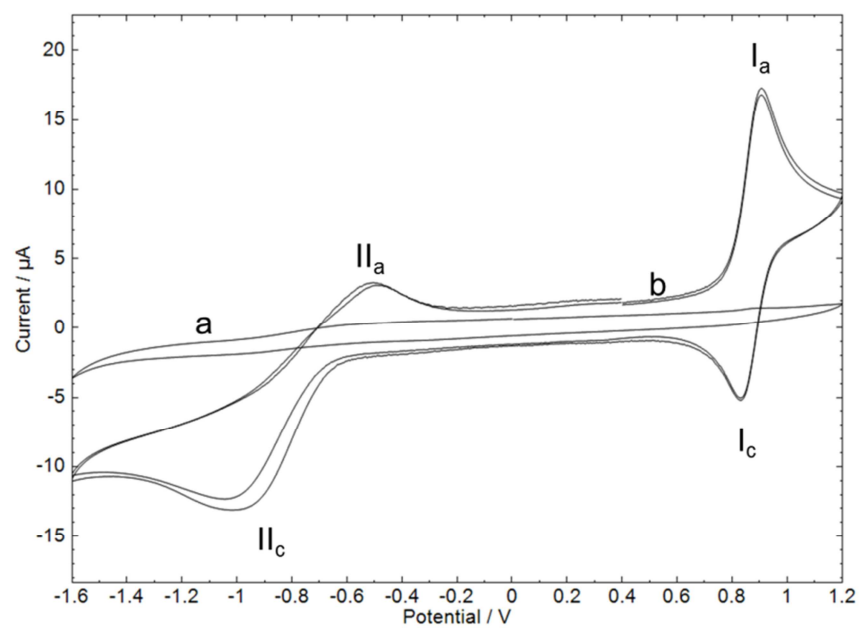


Figure 1

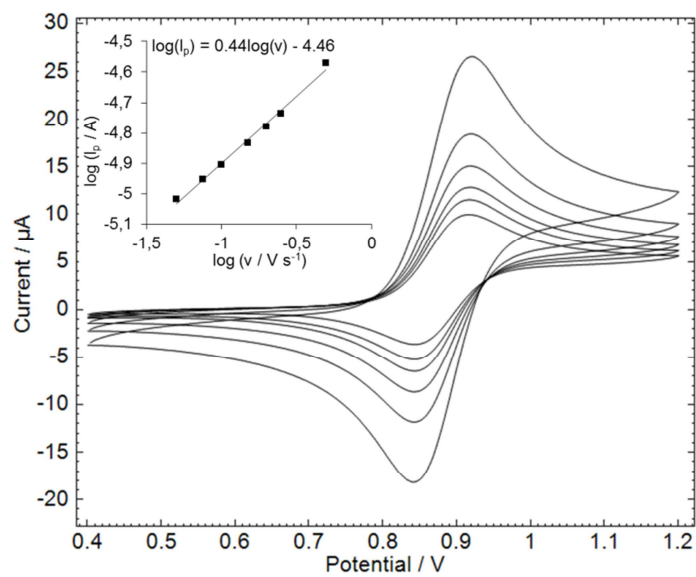
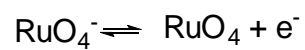


Figure 2



Scheme 1

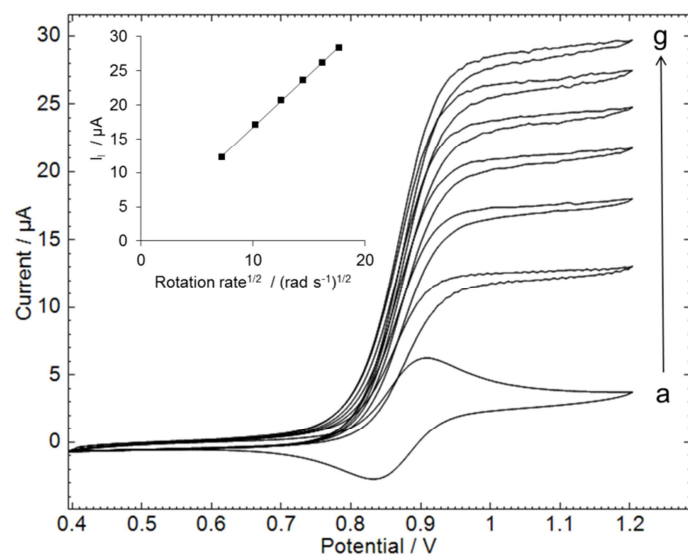
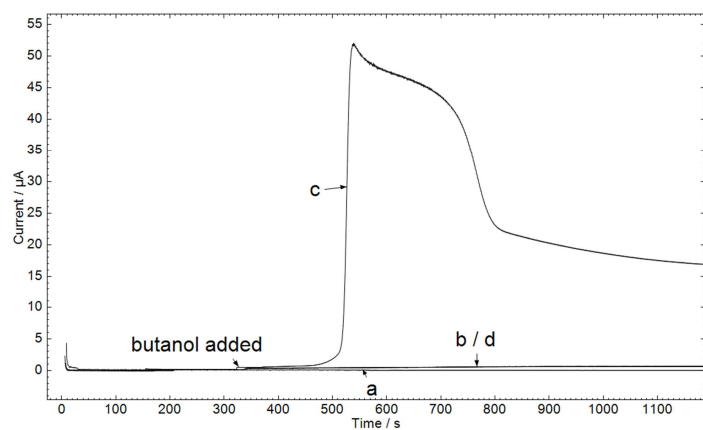


Figure 3



**Figure 4**

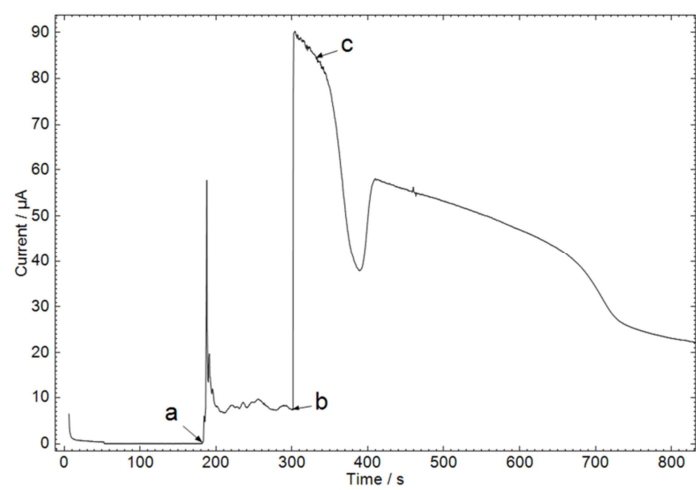
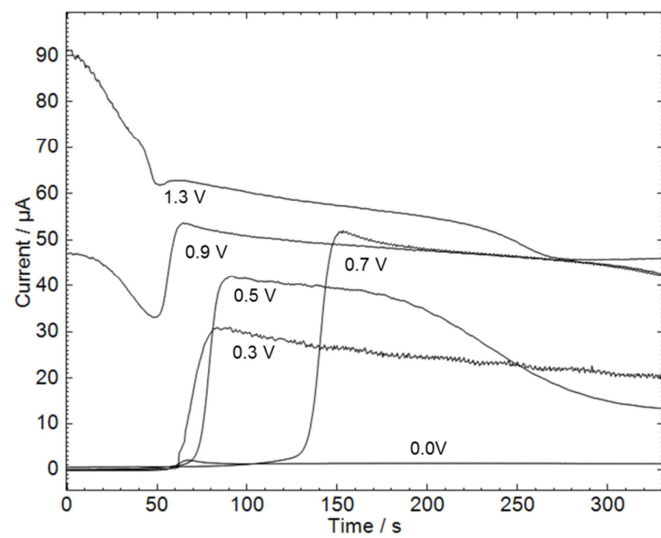
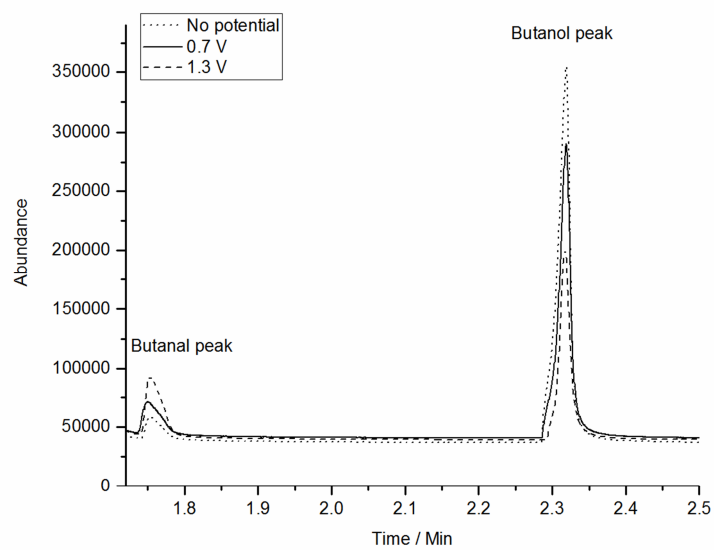


Figure 5



**Figure 6**



**Figure 7**