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# The activation of C—H bonds using an EmimAc/MWCNTs composite: a comparison of the composite used as electrolyte and electrode in aqueous media



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#### ABSTRACT

An EmimAc/MWCNTs composite was prepared and characterized through SEM and TEM. The MWCNTs were well dispersed after combining with alkaline EmimAc. The activity of the composite was demonstrated by CV and controlled potential electrolysis. The composite could be used independently as electrolyte or electrode and showed excellent activity toward the electro-oxidation of the C—H bond of benzylic systems, and did so at a lower oxidation potential than when using EmimAc or MWCNTs. After modification, the pH value of the composite was adjusted to the acid range, and the yield of aldehyde adducts obtained through electro-oxidation improved.

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#### 1. Introduction

The activation of unreactive C—H bonds serves as an important step in many synthetic transformations [1,2]. Over the past century, reports have appeared describing the role of inductive effects, conjugation, steric hindrance, and the introduction of directing groups to improve the selective activation of C—H bonds [3]. One attraction to this area of investigation focuses upon the electro-oxidative activation of a C—H bond to form a carbonyl unit [4–9]. Of course, the success of the chemistry requires optimization in order to determine a suitable solvent, electrolyte and electrode.

Room temperature ionic liquids (RTILs) and carbon nanotubes (CNTs) have attracted much interest [10,11]. RTILs are promising solvents and electrolytes in electrochemical applications because of their low volatility, high conductivities, and wide potential windows relative to conventional electrolytes [12]. While their high price and high viscosity limits widespread application, CNTs do offer significant advantages in electrochemical systems because of their unique structure and properties including, for example, large specific surface area, strong mechanical moduli and excellent

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chemical stability. Recently it was shown that some ILs exhibit unexpectedly strong interactions with CNTs through the formation of gels after the two have been ground together [13–15]. The resulting ILs/CNTs composites material were used as capacitors [16], sensors [17] and as a lubricant additive [18]. However few reports exist concerning their application to the electro-oxidation of C—H bonds to form aldehydes, a focal point of the present investigation.

In our previous work, ILs, especially imidazole ILs wherein the pH values ranged between 2 and 6, were shown to be a suitable solvent-electrolyte combination for the electro-oxidation of methyl-substituted aromatic compounds to the corresponding aldehydes. On the other hand, alkaline imidazole ILs such as 1-ethyl-3-methylimidazolium acetate (EmimAc), led preferentially to the formation of p-methoxybenzylalcohol (p-MeOBzOH) without further oxidation [9]. In an effort to expand the scope of the chemistry, we have explored the immobilization of the alkaline ILs with an objective being to decrease the amount of IL used and also facilitate the electro-oxidation of a C-H bond to a carbonyl unit. Greatly encouraged by the effectiveness of a recently reported composite dispersion reaction medium in eliminating the need to use large amounts of a supporting electrolyte in organic solvents [19], we chose to form a new composite, one consisting of EmimAc as the IL in combination with multi-walled carbon nanotubes (MWCNTs) and explored its use in aqueous reaction media. As described herein, the composite was able to function



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independently as electrolyte *and* also as the electrode, and to be applied to the electro-oxidative activation of C—H bonds. The composite showed excellent electro-oxidative activity and selectivity toward formation of carbonyl compounds and could easily be recovered and reused. In addition, adjustment of the pH value of the EmimAc/MWCNTs composite to the acid range, proved beneficial to the electro-oxidation to the carbonyl group, with yields for the conversion of *p*-methoxy toluene (*p*-MT) to *p*-methoxybenzaldehyde (*p*-MBA) improving from 55-63% to 87%.

# 2. Experimental section

#### 2.1. Chemicals and measurements

EmimAc was purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences), and used without further purification. MWCNTs, (97%, 40–60 nm in diameter) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (China) and vigorously stirred in 65% HNO<sub>3</sub> solution for 4 h at 423 K. Following treatment of the MWCNTs with nitric acid, they were filtered and repeatedly washed with water until the aqueous filtrate tested neutral, then dried at 353 K for 12 h before use. *p*-MT and *p*-methoxybenzyl alcohol were purchased from Aladdin (China), 1-methoxy-4-propylbenzene was purchased from Sigma Aldrich (Iceland), *p*-xylene was purchased from Sinopharm Chemical Reagent Co. Ltd (China). All the reagents were analytical grade.

Scanning electron microscopy (SEM) images were obtained using a Hitachi S4700 (Japan) system with an accelerating voltage of 15 kV. Before observation, the surface of the sample material was coated with a thin layer of gold. Transmission electron microscopy (TEM) was obtained by using JEM-2010Ex (Japan) with an accelerating voltage of 200 kV.

Cyclic voltammetry (CV) was carried out using a CHI 660D electrochemical workstation. A platinum sheet  $(1 \text{ cm} \times 0.5 \text{ cm})$  was used as the working electrode, a 2 cm  $\times$  2 cm platinum sheet as the counter electrode, and a platinum wire (0.5 mm diameter) electrode as the quasi-reference electrode. Except when noted, the CV measurements were performed at room temperature.

Each controlled potential electrolysis was performed in a 10 mL undivided electrochemical cell. The concentration of the aromatic substrate was 0.04 M. The electrolysis potential used for experiments conducted using different electrolytes was based on the oxidation peak potential recorded using CV. All the electrolysis experiments were performed at 323 K for 6 h while the solution was stirred using a magnetic stirrer. When the composite was used as the electrolyte, the 1 cm  $\times$  0.5 cm platinum sheet was used as the working electrode. For each controlled potential electrolytes for the electrolytes involving the use of different electrolytes for the electro-oxidative electrolysis of *p*-MT, 0.16g of EmimAc, 0.04g of MWCNTs and 0.2g of composite were independently

employed as the electrolyte. When the composite and the graphite electrode (5 mm diameter) were used as the working electrode,  $0.02 \text{ M LiClO}_4$  was used as the supporting electrolyte in an aqueous solution. The major products were detected using GC–MS (Thermo Fisher). The yields (Y) were determined by GC (Agilent 7890A) analysis.

The pH of the different electrolysis systems was measured using a PHS-3C acidometer (Shanghai REX, China) at room temperature.

#### 2.2. Preparation of EmimAc/MWCNTs

The MWCNTs were first mixed with EmimAc (the mass ratio of EmimAc to MWCNTs was 1:1, 2:1 and 4:1), using methylene chloride as a dispersant. The dispersion was stirred for 12 h at room temperature using a magnetic stirrer. Then, the resulting composite materials, referred to as EmimAc/MWCNTs, were dried at 353 K for 12 h.

Following electrolysis when the composite was used as the electrolyte, the composite was filtered, and the solid containing the EmimAc/MWCNTs composite was washed with ether. The filtrate containing the products and some desorbed EmimAc, was washed using distilled water. The product, contained in the organic phase, was detected by GC while the desorbed EmimAc was extracted using ether from the aqueous phase and combined with the solid, thereby constituting the recovered EmimAc/MWCNTs composite (marked as Re-EmimAc/MWCNTs).

## 2.3. Preparation of composite electrode

One hundred (100) mg of composite material, 1 mL of ethanol, 1 mL of distilled water and 100  $\mu$ L of Nafion solution (5 wt%) were combined to form a slurry. Then, 150  $\mu$ L of the slurry was added dropwise onto carbon paper (1 cm  $\times$  1 cm) and dried at room temperature for 12 h. After electrolysis, the resulting "composite electrode" was washed with distilled water, and dried at room temperature for reuse.

# 3. Results and discussion

The surface morphology of the nitrated MWCNTs and the EmimAc/MWCNTs composites were characterized by SEM (Fig. 1) and TEM (Fig. 2). After nitration, some of the ends of the MWCNTs were opened as evidenced by Fig. 1 a, but most of the tubes were tangled because of self-assembly and the nano-size effect [20]. After combining with the EmimAc, the MWCNTs became untangled (Fig. 1 b, d). The dispersion of the tubes was improved and the affinity of the ILs to the surface of the MWCNTs was ensured after they were combined due to the interaction between the electron deficient imidazolium cation and the  $\pi$ -electron-rich surface of the nitrated MWCNTs [21].



Fig. 1. SEM images of (a) the nitrated MWCNTs, and (b) EmimAc/MWCNTs (mass ratio = 4:1).



Fig. 2. TEM images of (c) the nitrated MWCNTs, and (d) EmimAc/MWCNTs (mass ratio=4:1).



Fig. 3. SEM images of EmimAc/MWCNTs with different mass loading (a) 1:1, (b) 2:1, (c) 4:1.

The SEM images of the composite material with differing mass loadings are shown in Fig. 3. With the increasing loading of the ILs (from 1:1 to 4:1), the MWCNTs became untangled and their selfassembly was attenuated so that most of the tubes were dispersed thereby ensuring the diffusion of the substrate and product.

In order to compare the oxidative performance of composites made from different IL loading materials, CVs of p-MT were recorded and are illustrated in Fig. 4. Clearly, there is an oxidation but no reduction peak in each of the electrolytes, indicating that the electro-oxidation of p-MT was irreversible in each case. Compared with the oxidation peak potential for p-MT in EmimAc (1.35 V), the peak potential recorded in the composite material

EmimAc/MWCNTs (4:1) was shifted to less positive values (viz., to <1.3 V), indicating that the electro-oxidative process of *p*-MT could be carried out at a lower potential and the total energy consumption might thereby be reduced. Additionally, the oxidation peak current recorded in the composite material EmimAc/MWCNTs (4:1) was approximately twice that recorded using EmimAc alone (1.5 vs 0.76 mA). The EmimAc/MWCNTs composite material showed improved activity toward the electro-oxidation of *p*-MT. Regrettably, the CV of *p*-MT in the MWCNTs could not be recorded because the MWCNTs rapidly precipitated during the experiment.

The CVs of p-MT, p-methoxybenzyl alcohol, 1-methoxy-4propylbenzene, and p-xylene each recorded in the EmimAc/ MWCNTs (4:1) composite are depicted in Fig. 5. The effect of



**Fig. 4.** The cyclic voltammograms of *p*-MT in different electrolytes. (a) EmimAc /  $H_2O$ ; (b) *p*-MT in EmimAc /  $H_2O$ ; (c) *p*-MT in EmimAc/MWCNTs(1:1) /  $H_2O$ ; (d) *p*-MT in EmimAc/MWCNTs(2:1) /  $H_2O$ ; (e) *p*-MT in EmimAc/MWCNTs(4:1) /  $H_2O$ . The insert highlights the oxidation curves between 0.9 and 1.6V.  $\upsilon$  = 50 mV/s.



**Fig. 5.** The cyclic voltammograms of *p*-MT, *p*-methoxybenzyl alcohol, 1-methoxy-4-propylbenzene and *p*-xylene in the composite EmimAc/MWCNTs (4:1).



**Fig. 6.** The cyclic voltammograms of *p*-MT in different electrolytes and recorded at different temperatures. For (a) and (b), *p*-MT CVs recorded in 0.02 moldm<sup>3</sup> LiClO<sub>4</sub> /  $H_2O$  at room temperature and 323 K, respectively; For (c) and (d), *p*-MT CVs recorded in EmimAc /  $H_2O$  at room temperature and 323 K, respectively; For (e) and (f), *p*-MT CVs recorded in EmimAc/MWCNTs(4:1) /  $H_2O$  at room temperature and 323 K, respectively. The insert illustrates the oxidation curves between 0.8 and 1.6 V.

temperature on the electro-oxidation process was addressed by recording the CV of p-MT, first at room temperature and then at 323 K, and repeating the process in three different electrolytic media, viz., 0.02 M LiClO<sub>4</sub>, pure EmimAc, and the composite EmimAc/MWCNTs (4:1), respectively. The results (Fig. 6) clearly show that the current increases each time the temperature is increased, the same being true in each of the three reaction media (compare, for example, curve a with b, c with d, and e with f). Compared to LiClO<sub>4</sub> (curve a to b), both of the EmimAc containing systems were more sensitive to the temperature increase (curve c to d, curve e to f). Interestingly, while the oxidation peak current for the electro-oxidation of p-MT in pure EmimAc increased markedly when the temperature was raised, the oxidation process led preferentially to the formation of p-MeOBzOH [9].

Since the oxidation peak current for the electro-oxidation of *p*-MT in the composite EmimAc/MWCNTs (4:1) was larger and the oxidation peak potential was lower than that in the pure EmimAc at 323 K, we chose to conduct the following electrolyses at 323 K.

The results of controlled potential electrolyses of p-MT carried out in different electrolytic media or at different electrodes are shown in Fig. 7. Using a graphite electrode, 8% of dimer was detected. Gratifyingly, it is clear that when the composite material EmimAc/MWCNTs (4:1) is used as the electrolyte or the electrode, the electro-oxidation of p-MT to form p-MBA is significantly



**Fig. 7.** The electrolysis products of *p*-MT in differing aqueous solutions. (a) EmimAc electrolyte; (b) MWCNTs electrolyte; (c) EmimAc/MWCNTs (4:1) electrolyte; (d) Re-EmimAc/MWCNTs electrolyte; (e) EmimAc/MWCNTs (4:1) electrode; (f) graphite electrode.

#### Table 1

The pH of the aqueous solutions of different electrolytes.

solution	pH
EmimAc $(0.16 g) + H_2O (5 mL)$	7.28
MWCNT $(0.04 g) + H_2O (5 mL)$	5.0
EmimAc/MWCNT $(0.2 g) + H_2O (5 mL)$	6.4



Fig. 8. Recycling the composite electrode in the electro-oxidation of *p*-MT.

improved. Thus, the yield of *p*-MBA increased from 55-63% to 87% when the EmimAc or the MWCNTs was replaced by EmimAc/MWCNTs (4:1).

This outcome contrasts with our previous work when alkaline ILs were used as electrolytes. Under alkaline conditions, the oxidation led preferentially to the formation of *p*-methoxybenzyl alcohol without further oxidation to the aldehyde [9]. To explore these contrasting results, we measured the pH of aqueous solutions of EmimAc, the MWCNTs, and the combination of the two (4:1). The results, listed in Table 1, show that the pH value of the combination is in the acid range, which is beneficial for the electro-oxidation to the carbonyl group.

When the composite EmimAc/MWCNTs (4:1) was used as the working electrode, an emulsion appeared because of the poor solubility of the substrate in water. The product, *p*-MBA, is more soluble in water than *p*-MT. This proves beneficial to the diffusion of *p*-MBA, formed near the electrode surface, into the bulk solution as the reaction occurs, thereby protecting it from over-oxidation.

To study the electrochemical stability of the composite material when the EmimAc/MWCNTs composite was used as electrolyte, the EmimAc/MWCNTs were recovered and reused as electrolyte for the activation of the C-H bond of *p*-MT; using the recovered material a yield of 76% of *p*-MBA was obtained (column d of Fig. 7). The result of carrying out a controlled potential electrolysis of *p*-MT using the recycled composite electrode is shown in Fig. 8. After 8 cycles, the yield of the major product, *p*-MBA, began to decrease while oxidation to the alcohol increased. We conclude that *both* the recycled electrolyte and electrode display excellent electrochemical activity for the electro-oxidation.

# 4. Conclusion

The composite material, EmimAc/MWCNTs, was prepared and used independently as electrolyte and electrode for the electrooxidation of benzylic C—H bonds to the corresponding carbonyl group. With the synergistic function of the EmimAc and MWCNTs, the activity of the resulting composite material improved. The chemistry could be carried out in aqueous solutions. Whether the composite material EmimAc/MWCNTs (4:1) was used as electrolyte or electrode, the oxidation peak potentials for the electrooxidation of *p*-MT decreased (i.e. became less positive), which in principle reduces the total energy consumption. When the composite material was used as the electrolyte, we avoided the need for additional supporting electrolyte. We are pleased to note that the composite electrode was more easily recovered and reused than the pure ILs, and we recommend use of the composite electrode for the electro-oxidation of p-MT. The recycling experiments demonstrated the excellent electrochemical stability for the composite EmimAc/MWCNTs. Thus, ILs with alkaline properties can be used for the oxidation of benzylic C-H bonds when combined with MWCNTs.

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