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ORIGINAL PAPER

Electroreduction of carbonyl compounds at a Ti/ceramic TiO_2 cathode

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Abstract The use of Ti/ceramic TiO_2 cathode as an effective cathode material for the reduction of two ketones—cyclohexanone and benzalacetone (BA) are highlighted. Galvanostatic reduction of these ketones gave exclusively cyclohexanol and benzyl acetone (4-phenyl 2-butanone) as the corresponding hydrogenated products, as characterized from their boiling points and nmr spectra. Higher product yields were observed as compared to the reduction of the ketones at conventional cathode materials like lead under identical experimental conditions. Best conditions for the formation of products have been identified based on current density, temperature and acid strength. Cyclic voltammetry indicates a mechanism involving heterogeneous redox catalysis involving the surface fixed redox groups Ti^{4+}/Ti^{3+}. The reaction can be conveniently scaled up.

Keywords Electroreduction · Modified electrode · Carbonyl compounds · Galvanostatic electrolysis · Cyclic voltammetry · Heterogeneous redox catalysis

1 Introduction

The Ti/ceramic TiO_2 cathode has been found to be very effective in the reduction of the nitro and nitroso groups and the electro catalytic reduction of a number of nitro and nitroso compounds has been reported [1–7]. Advantages include high turn over factor of the electrode and electro catalytic reduction of the nitro and nitroso group at the electrode surface. Maleic, fumaric, oxalic and pthalic acids were also reduced to their corresponding products in very high yields at this cathode material [3, 8, 9]. This paper reports the reduction of two ketones, cyclohexanone and benzalacetone (BA), at this electrode.

Meerwein–Ponndorf–Verley reduction of cyclohexanone, in the presence of propane-2-ol and zirconia and its mixed oxide, lanthanum or aluminium isopropoxide, as catalysts, at 150–300 °C yields cyclohexanol [10, 11]. However, the metal alkoxide catalysts are homogeneous, create problems during separation and are not reusable.

The liquid-phase reduction of α,β-unsaturated ketones like benzalacetone ($C_6H_5CH{=}CHCOCH_3$) to the corresponding α,β-unsaturated alcohols has been observed with chemoselectivity greater than 60% on gold-supported catalysts—Au/Fe_2O_3 and Au/Al_2O_3 [12]. In the hydrogenation of 3-penten-2-one with Au/Fe_2O_3, however, the saturated ketone is the main reaction product and the selectivity toward the formation of the unsaturated alcohol is 15% at conversion >90%. The absence of bulky substituents on the conjugated C=C double bond favors its adsorption on the catalytic sites, leading to the formation of the saturated carbonyl compounds as the main reaction product. Selective hydrogenation of the carbonyl group can be achieved using noble metal catalysts in the case of α,β-unsaturated aldehydes but with α,β-unsaturated ketones, it is always the saturated ketone that is formed [13].

Benzylacetone can be prepared by hydrogenating benzylideneacetone in the presence of a palladium catalyst on activated carbon and/or a palladium catalyst on aluminum oxide[14]. Taran et al. have reported the cathodic hydrogenation of benzalacetone to benzylacetone at platinized platinum [15].

Cyclohexanol is an intermediate in the production of adipic acid (for use in nylon 66) and cyclohexanone which is converted to caprolactam (for nylon 6). It is used as a solvent and a dry cleaning material. It is used in making

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soaps and detergents and is also used as an intermediate for pharmaceuticals, plasticizers, perfumery, cement, rubber chemicals, cyclohexylamine and insecticides [16, 17]. Benzylacetone is a harmless perfumery chemical that finds usage in the formulations of fragrances.

2 Experimental

2.1 Solvents and chemicals

Cyclohexanone (S D Fine), benzalacetone (Sisco), methanol (E Merck) and sulphuric acid (Merck) of AR quality were used. Water used in all experiments was twice distilled.

2.2 Instrumentation, electrodes and cell assembly

A regulated d.c power supply (Model L3220, Aplab, India) was employed as the constant current source. Cyclic voltammetric set up was the same as employed earlier [3–6].

The procedure employed for the preparation of Ti/ceramic TiO_2 cathode employed for galvanostatic and cyclic voltammetry studies was identical to that employed earlier [3–7]. An expanded Ti/ceramic TiO_2 electrode of area 0.86 dm^2 (or lead of area 0.89 dm^2) was used as the cathode while lead of area 0.80 dm^2 was used as anode (placed inside a ceramic porous pot as diaphragm) for galvanostatic electrolysis. A Ti/ceramic TiO_2 strip of 0.196 cm^2 exposed area was used as the working electrode in the cyclic voltammetry. An aqueous SCE and a platinum foil served as the reference and counter electrodes, respectively. A 1 L beaker was employed for galvanostatic studies and a glass cell (holding around 25 mL solution) with provision for introducing working, reference and counter electrodes was employed for cyclic voltammetry. Either 50% methanolic 1 M H_2SO_4 or 1 M H_2SO_4 consisting of the required amount of the ketone was used as the catholyte for both galvanostatic electrolysis and cyclic voltammetry while 50% methanolic 1 M H_2SO_4 or 1 M H_2SO_4 (based on solubility considerations) was the anolyte during galvanostatic studies. The reactions were carried out in the current density range 1.0–7.5 A dm^{-2} and in the temperature range 40–60 °C. The quantity of electricity consumed was 2 faraday mol^{-1} of cyclohexanone or benzalacetone.

2.3 Product work up and characterisation

After completion of electrolysis, in the case of cyclohexanone, unreduced cyclohexanone was precipitated as the bisulphite adduct by adding sodium bisulphite. The filtrate was ether extracted and evaporated off to give cyclohexanol, a colourless liquid. In the case of benzalacetone, the electrolysed solution was ether extracted to remove unreduced benzalacetone and then extracted with carbon tetrachloride, which on evaporation yielded benzylacetone, a colourless liquid. The isolated yields of the products were found. The boiling points of the products were determined and compared with the corresponding literature values. H^1 NMR spectra ($CDCl_3$) of the products were recorded using Bruker Avance – 400 MHz FT NMR spectrometer (Fallandem, Switzerland) and compared with those for cyclohexanol and benzylacetone reported in the literature.

3 Results and discussion

3.1 Galvanostatic electrolysis

3.1.1 Cyclohexanone

The results of galvanostatic electrolysis data on the reduction of cyclohexanone under varying conditions of current density, acid strength and temperature at a Ti/ceramic TiO_2 cathode are listed in Table 1.

The H_2SO_4 strength was maintained at 1 M for all the experiments since resin formation occurred at higher acid strengths. At a current density of 1.0 A dm^{-2} and a temperature of 40 °C, best yield of cyclohexanol is observed (S 1). Higher current densities do not favour the reaction, possibly due to competing reactions. Lower yields at higher temperatures are most likely due to evaporation loss. The yield is considerably reduced at a Pb cathode indicating the electrocatalytic nature of Ti/ceramic TiO_2 cathode.

Table 1 Galvanostatic electrolysis data on the reduction of cyclohexanone in 1 M H_2SO_4 at a Ti/ceramic TiO_2 cathode

S	Wt of cyclohexanone (g)	J (A dm^{-2})	*T* (°C)	Wt of cyclohexanol (g)	Yield[b] (%)
1	10	1.0	40	9.4	91.8
2	10	2.0	40	8.9	67.6
3	10	3.0	40	8.2	60.3
4	10	4.0	40	7.4	73.0
5	10	5.0	40	6.6	64.7
6	10	7.5	40	6.3	61.5
7	10	1.0	50	7.7	75.1
8	10	1.0	60	6.4	62.6
9[a]	10	1.0	40	7.8	76.1

[a] Pb cathode

[b] Isolated product yield

The product was a colorless liquid having camphor like odour with a boiling point of 160−161 °C which matched with the value for cyclohexanol (Lit value 161 °C [18]). H^1 NMR spectrum ($CDCl_3$) of the product showed peaks at $\delta = 1$–2 (m, 10H), 2.63 (s, 1H) and 3.58 (s, 1H). This is in conformity with literature data on the NMR of cyclohexanol [19].

3.1.2 Benzalacetone

The results of galvanostatic electrolysis carried out on BA under varying conditions of current density, acid strength and temperature are listed in Table 2.

The best reduction of benzalacetone is observed at a current density of 4 A dm^{-2}. Higher current densities favour competitive hydrogen evolution thereby reducing the yield considerably. Also, the effect of T (S.No. 4, 7, 8) shows that 40 °C is the most suitable condition. Loss of methanol is likely to reduce the product yield of benzylacetone at higher *T*. In general, the yield in the reduction of benzalacetone is considerably lower as compared with the other compounds including cyclohexanone, maleic and fumaric acids and the nitro and nitroso compounds. Steric effects due to the large size of the compound, methanol loss due to evaporation and adsorption of methanol on the electrode surface may be responsible for the lower yield.

Benzylacetone (4-phenyl 2-butanone) is the product, a colourless liquid that boiled at 234 °C (Lit value 235 °C [20]). In general for a double bond in conjugation with a carbonyl, it is always the double bond that is reduced. Further, the product does not decolorize bromine water indicating the absence of a double bond. Also the product gives semicarbazone (m.p. 131 °C, Lit value 131 °C [21]) on reaction with semicarbazide indicating that the carbonyl group is not reduced under the present electrochemical conditions.

Table 2 Galvanostatic electrolysis data on the reduction of benzalacetone in 50% methanolic 1 M H_2SO_4 at a Ti/ceramic TiO_2 cathode

S	Wt of benzal-acetone (g)	J (A dm^{-2})	*T* (°C)	Wt of benzyl-acetone (g)	Yield[b] (%)
1	10	1.0	40	7.3	50.3
2	10	2.0	40	7.6	52.3
3	10	3.0	40	8.1	56.2
4	10	4.0	40	9.0	62.1
5	10	5.0	40	8.3	57.2
6	10	7.5	40	6.9	47.5
7	10	4.0	50	7.6	52.3
8	10	4.0	60	6.4	44.4
9[a]	10	4.0	40	7.7	53.3

[a] Pb cathode

[b] Isolated product yield

H^1 NMR spectra ($CDCl_3$) of the product showed peaks at $\delta = 2.1$(s, 3H), 2.75(t, 2H), 2.91(t, 2H) and 7.1–7.3(m, 5H). This is in conformity with literature data on the NMR of benzylacetone [19].

3.2 Cyclic voltammetric studies

A typical cyclic voltammogram for a Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 at different sweep rates is shown in Fig. 1.

A cathodic peak is seen at around −0.57 V and the corresponding anodic peak is seen at around −0.52 V. These peaks are attributed to the following redox reaction:

$$TiO_2 + H_2O + H^+ + e^- \rightleftharpoons Ti(OH)_3 \quad (1)$$

It was earlier reported that, in the presence of added nitro and nitroso compound, the cathodic peak height increased with simultaneous disappearance of the anodic

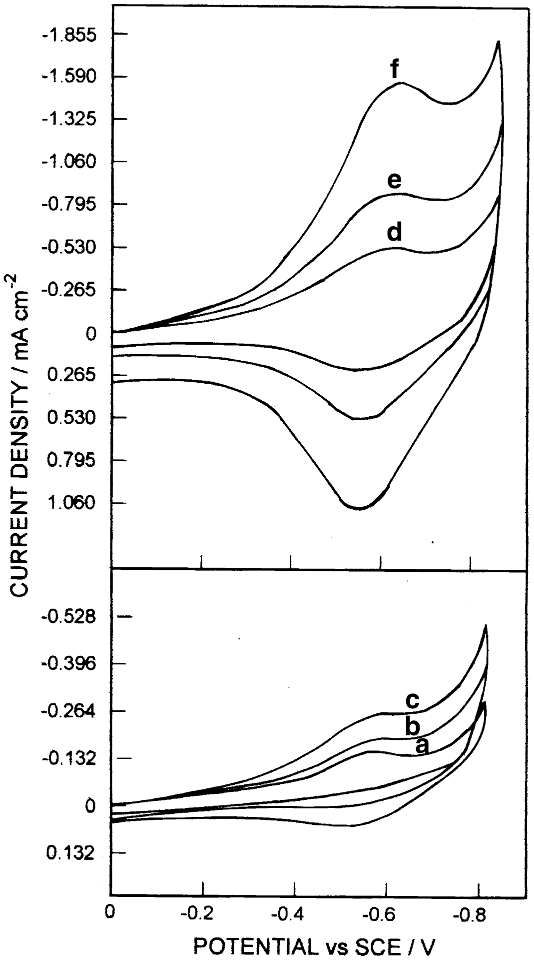


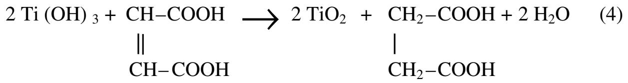
Fig. 1 Cyclic voltammetry behaviour of Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 at (**a**) 5 (**b**) 10 (**c**) 20 (**d**) 50 (**e**) 100 (**f**) 200 mV s^{-1}

peak [4–7]. This is due to chemical reduction of the nitro and nitroso compounds by the electrogenerated Ti^{3+}. This is represented in the equations:

$$6Ti(OH)_3 + RNO_2 \rightarrow 6TiO_2 + RNH_2 + 8H_2O \quad (2)$$

$$4Ti(OH)_3 + RNO \rightarrow 4TiO_2 + RNH_2 + 5H_2O \quad (3)$$

A similar effect was seen for the addition of maleic acid and fumaric acid [8, 9] and the reaction can be represented as



$$2\,Ti(OH)_3 + \begin{array}{c} CH{-}COOH \\ \| \\ CH{-}COOH \end{array} \longrightarrow 2\,TiO_2 + \begin{array}{c} CH_2{-}COOH \\ | \\ CH_2{-}COOH \end{array} + 2\,H_2O \quad (4)$$

The effect of added cyclohexanone on the response of the Ti/ceramic TiO_2 cathode in 1 M H_2SO_4 at different sweep rates is given in Fig. 2. At lower sweep rates (5–10 mV s^{-1}), the cathodic peak height increases and the anodic peak disappears altogether. However, complete disappearance of the anodic peak is not seen at high sweep rates. This is because, the Ti^{3+} formed upon electroreduction of Ti^{4+}, does not have sufficient time to react with cyclohexanone completely in the chemical step in the time scales of higher sweep rates.

The effect of addition of 1.7 and 107 mM cyclohexanone on the cyclic voltammetric response of Ti/ceramic TiO_2 cathode at 5 mV s^{-1} sweep rate is shown in Fig. 3.

At both concentrations, complete disappearance of the anodic peak is seen, and much higher currents are observed at 107 mM due to the higher concentration of cyclohexanone and hence higher catalysis. Similarly to the effects observed for the nitro and nitroso compounds, these compounds were indirectly reduced by the electrogenerated Ti^{3+} regenerating Ti^{4+} indicating heterogeneous redox catalysis by the surface fixed redox couple Ti^{4+}/Ti^{3+}. The redox catalytic reaction can be represented as follows (analogous to reactions 2, 3 and 4 above):

$$2Ti(OH)_3 + C_6H_{10}O \rightarrow 2TiO_2 + C_6H_{11}OH + 2H_2O \quad (5)$$

The typical cyclic voltammetry response for the behaviour of Ti/ceramic TiO_2 cathode in 50% (v/v) methanolic 1 M H_2SO_4 at different sweep rates is shown in Fig. 4.

A response similar to that observed in Fig. 1 is seen, though the peaks are less well defined, especially at lower sweep rates probably due to methanol adsorption on the electrode surface. Equation 1 also holds good here.

The effect of added benzalacetone (3.3 mM) on the response of the Ti/ceramic TiO_2 cathode in 50% (v/v) methanolic 1 M H_2SO_4 at different sweep rates is shown in Fig. 5.

It can be inferred from Fig. 5 that the reaction between the electrogenerated Ti^{3+} and benzalacetone takes place in the time scale of lower sweep rates (5–20 mV s^{-1}) as seen from the complete disappearance of the anodic peak. However, at higher sweep rates, the anodic peak still persists indicating that the chemical reaction does not occur sufficiently. This observation is similar to that seen for cyclohexanone reduction earlier in this paper. The heterogeneous redox catalytic reaction is represented as

$$2Ti(OH)_3 + C_6H_5CH = CHCOCH_3 \rightarrow 2TiO_2 + C_6H_5CH_2CH_2COCH_3 + 2H_2O \quad (6)$$

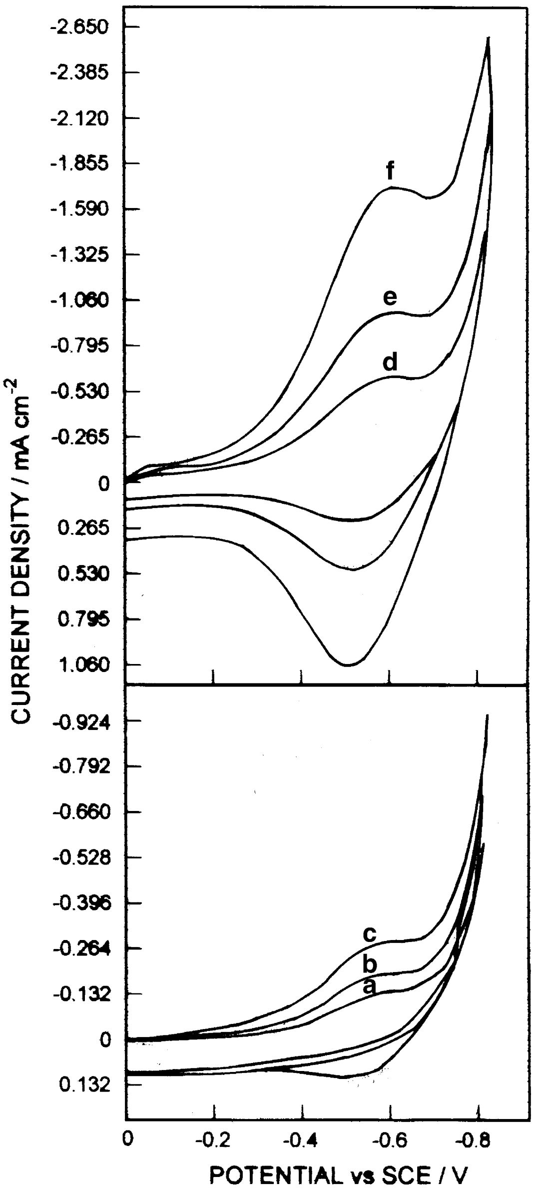


Fig. 2 Effect of added cyclohexanone (3.3 mM) on the response of the Ti/ceramic TiO_2 cathode in1 M H_2SO_4 at (**a**) 5 (**b**) 10 (**c**) 20 (**d**) 50 (**e**) 100 (**f**) 200 mV s^{-1}

The effect of added benzalacetone (106 mM) on the response of the Ti/ceramic TiO_2 cathode in 50% (v/v) methanolic 1 M H_2SO_4 at different sweep rates is shown in

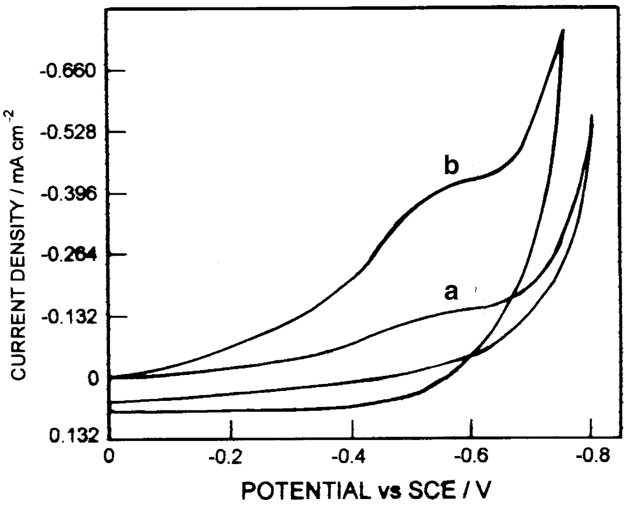


Fig. 3 Effect of addition of 1.7 (**a**) and 107 (**b**) mM of cyclohexanone on the cyclic voltammetric response of Ti/ceramic TiO_2 cathode at 5 mV s^{-1}

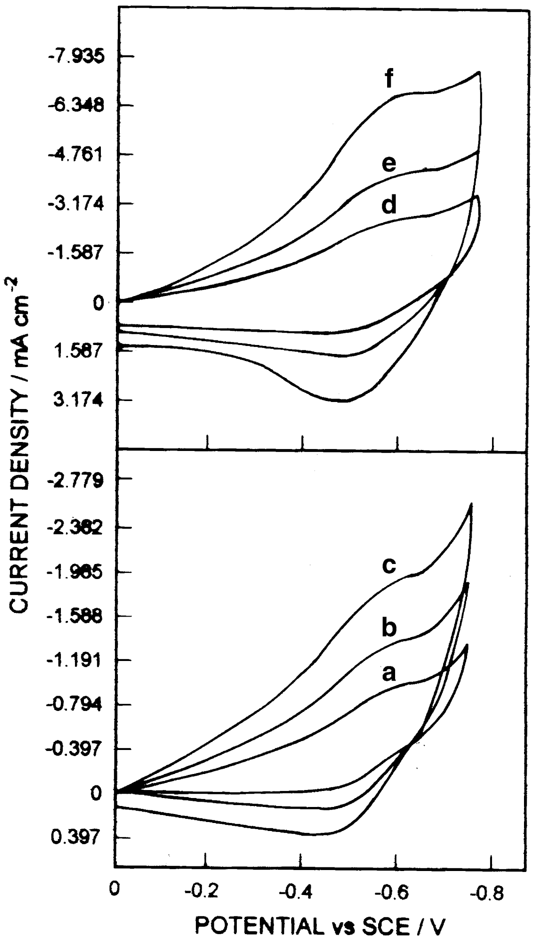


Fig. 4 Cyclic voltammetry behaviour of Ti/ceramic TiO_2 cathode in 50% methanolic 1 M H_2SO_4 at (**a**) 5 (**b**) 10 (**c**) 20 (**d**) 50 (**e**) 100 (**f**) 200 mV s^{-1}

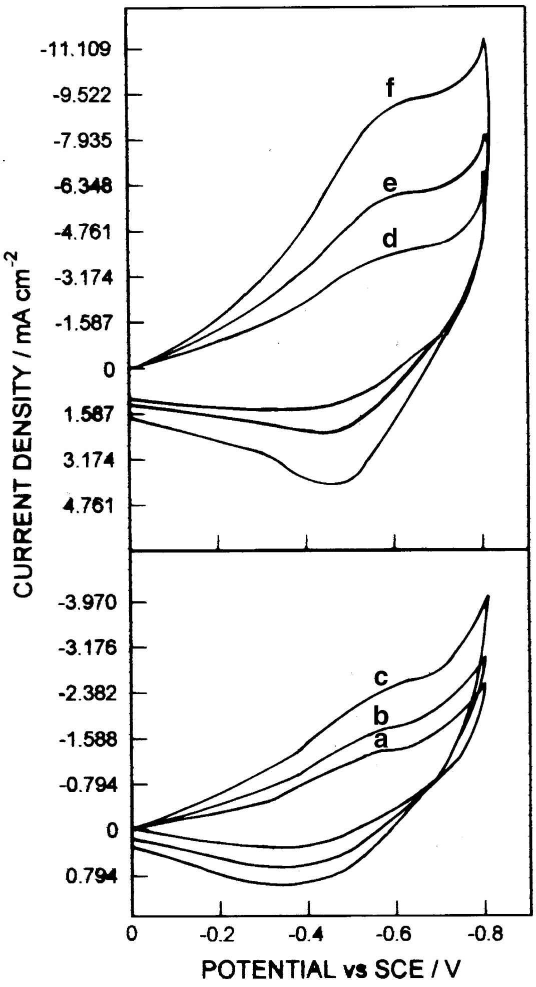


Fig. 5 Effect of added benzalacetone (3.3 mM) on the response of the Ti/ceramic TiO_2 cathode in 50% (v/v) methanolic 1 M H_2SO_4 at (**a**) 5 (**b**) 10 (**c**) 20 (**d**) 50 (**e**) 100 (**f**) 200 mV s^{-1}

Fig. 6. A comparison with Fig. 5 indicates that at higher concentrations of benzalacetone, the chemical reaction is faster, even at higher sweep rates.

4 Conclusion

The Ti/ceramic TiO_2 cathode is very effective for the reduction of ketones—cyclohexanone and benzalacetone to cyclohexanol and benzylacetone in sulphuric acid medium. Higher isolated product yields were observed as compared to those at conventional cathodes like Pb. The reaction can be conveniently scaled up. Indirect reduction of these compounds is observed by the electrogenerated Ti^{3+} which chemically reduces the substrate, thereby regenerating Ti^{4+}. Hence there is heterogeneous redox catalysis by the surface fixed redox group as seen from cyclic voltammetric studies.

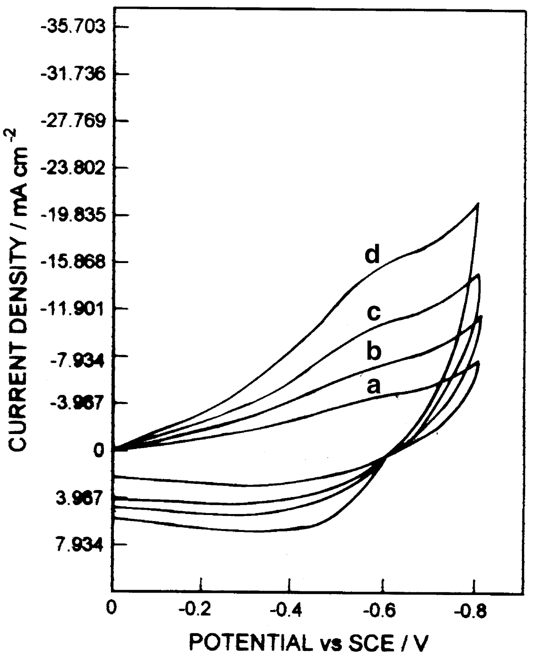


Fig. 6 Effect of added benzalacetone (106 mM) on the response of the Ti/ceramic TiO_2 cathode in 50%(v/v) methanolic 1 M H_2SO_4 at (**a**) 20 (**b**) 50 (**c**)100 (**d**) 200 mV s^{-1}

References

1. Beck F, Gabriel W (1986) Dechema Monographian 102:339
2. Beck F, Gabriel W (2003) Angewandte Chemie 24:771
3. Ravichandran C, Vasudevan D, Anantharaman PN (1993) J Electrochem Soc India 42–43:193
4. Ravichandran C, Vasudevan D, Anantharaman PN (1992) J Appl Electrochem 22:179, 1192
5. Vasudevan D, Anantharaman PN (1996) J Appl Electrochem 26:767
6. Vasudevan D, Chellammal S, Anantharaman PN (1991) J Appl Electrochem 21:839
7. Vasudevan D, Anantharaman PN (1994) J Appl Electrochem 24:559
8. Vasudevan D (1995) J Appl Electrochem 25:176
9. Joseph Kennady C (1994) PhD thesis
10. Ranga Rao G, Sahu HR, Mishra BG (2003) React Kinet Catal Lett 78(1):151
11. Kumbhar PS, Valente JS, Lopez J, Figueras F (1998) Chem Commun 535
12. Milone C, Ingoglia R, Pistone A, Neri G, Frusteri F, Galvagno S (2004) J Catal 222:348
13. Milone C, Ingoglia R, Tropeano ML, Neri G, Galvagno S (2003) Chem Commun 868
14. United States Patent 20020055656
15. Taran LA, Beresina SI, Smolentseva LG, Likhachev VA (1974) Soviet Electrochem 10:749; (1973) 9:756
16. Budavari S (ed) (1989) An encyclopedia of chemicals, drugs and biologicals, 11th edn. Merck and Co, New Jersey, p 2729
17. Gerhartz W (ed) (1987) Ullmann's encyclopedia of industrial chemistry, vol A8, 5th edn. VCH, Weinheim
18. Dictionary of Organic Compounds (1996) vol 2, 6th edn. Chapman and Hall, 9.1637
19. SDBS, Spectral Database for Organic Compounds, SDBS, National Institute of Advanced Industrial Science and Technology, AIST, Japan
20. Aldrich Advancing Science (2005–2006) Sigma Aldrich Company, p 1841
21. Challenger F, Bott TH (1925) J Chem Soc Trans 127:1039