



# **ELECTROSYNTHESIS OF BENZOIC ACID DERIVATIVES AND ITS POLYMERS IN THE PRESENCE OF SUPEROXIDE USING FUEL CELL TECHNOLOGY**

**MEETA TRIVEDI\* and RAJNI MATHUR<sup>a</sup>**

Department of Polymer Engineering, IIT Roorkee, Saharanpur Campus, SAHARANPUR (U.P.) INDIA

<sup>a</sup>Department of Chemistry, Govt. P. G. College, DAUSA (Raj.) INDIA

## **ABSTRACT**

Hydroxy toluene and nitro toluene are not easily oxidized. Nitro and hydroxy groups inhibit oxidation in the presence of super oxide.<sup>1-3</sup> Super oxide is generated in aprotic solvent by the reduction of molecular oxygen electrochemically in the potential range -0.85 to 0.90 versus SCE. Super oxide oxidized toluene and its derivatives. Besides case of oxidation of toluene and its derivatives, work could be extended further in persu oxygen reduction studies on non metallic surface such as different type of carbon and graphite with a view to understand the reaction mechanism and possible applications to fuel cell technology.<sup>4-6</sup> A fuel cell is a device that convert the electricity through a chemical reaction with or another oxidizing agent. A fuel cell operates electrochemically or more literally chemico electricity. This cell is actually a reactor, it consist of two electronic conductor electrodes separated by an ionic conducting electrolyte with provision for the continuous movement of fuel oxidant and reaction product into and out of the cell. The fuel is carbon rod the electrolyte tetramethyl ammonium bromide and the oxidant is superoxide. The superoxide ion move to carbon electron is accepted by monomer and finally give polymer.

**Key words:** Fuel cell, Polymerization, Graphite, Super oxide.

## **INTRODUCTION**

The electrochemical generation of super oxide anion and subsequent electro-oxidation in situ is found to be advantageous and easy even the conventional techniques oxidation of toluene, Hydroxy toluene and nitro toluene is of importance in organic chemistry because of the many uses of benzoic acid in the presence of super oxide oxidation takes place very easily and percentage yield an 66.3%, 64.4%, 65%, 55.2% abd 59.8% for toluene, o-hydroxytoluene, p-nitrotoluene, respectively. The products are isolated and characterized by IR, <sup>1</sup>H NMR, molecular weight and melting points. In present investigation, we further prepare polymers. A fuel cell is device that convert the electricity through

---

\* Author for correspondence; E-mail: [rajni1965@yahoo.co.in](mailto:rajni1965@yahoo.co.in)

chemical reaction with oxygen or other oxidizing agent. In a cell, which consist of two electronic conductor electrodes separated by an ionic conducting electrolyte with provision for the continuous movement of fuel oxidant and reaction product in to and out of the cell. The fuel is a carbon rod and electrolyte tetra methyl ammonium halide, perchlorate, Borate and oxidant is superoxide. Super oxide is a nucleophilic agent and its property to act as oxidizing agent is much more equivocal. The superoxide anion in aprotic solvent has been generated by the electrolytic reduction of molecular oxygen at mercury pool cathode. The ion so generated oxidizes the carbon of the electrode liberating four electrons, which induce polymerization via radical on yielding desired polymer.

## **EXPERIMENTAL**

### **Material**

Toluene, o- and p-hydroxy toluene, o- and p-nitro toluene, tetra methyl ammonium borate, acetonitrile were used as such.

### **Cell assembly**

A beaker (500 mL) was used as the undivided cell. Mercury pool (working area  $35.26 \text{ cm}^3$ ) was used as cathode and carbon rod was the anode. The electrolyte consisted of 150 mL acetonitrile solution, which was 2.5 mM w.r.t. substrate and 0.05 M w.r.t. tetra methyl ammonium bromide. The mixture was maintained at  $25 \pm 2^\circ\text{C}$ . Air was bubbled and mixture was magnetically stirred through out the reaction. Electrolysis was carried out by passing a constant current (100, 200 and 300 mA) from a regulated D.C. power supply.

After passing the current for three hours, the mixture was filtered and acetonitrile removed under vacuum distillation. The residue thus obtained was extracted with chloroform and the solvent evaporated under vacuum. The product gave single spot on TLC.

The electrochemical polymerization was carried out in a single cell compartment without separating the mercury pool cathode and carbon anode. Superoxide ion is easily generated from the reduction of molecular oxygen which gets dissolved in aprotic solvents at  $-0.85$  to  $-0.90 \text{ V}$  versus SCE at mercury pool cathode in the presence of quaternary ammonium salt.

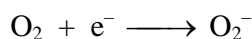
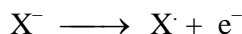
## **RESULTS AND DISCUSSION**

The application of electrochemical reduction of molecular oxygen to superoxide anion generated in situ has been utilized in the synthesis of benzoic acid and its derivative.

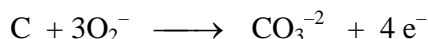
The superoxide anion was generated satisfactorily at mercury pool at  $-0.85$   $-0.90$  V by electrochemical reduction of molecular oxygen which gets dissolved in aerated acetonitrile solution containing tetra methyl ammonium bromide. The toluene, o-, p- hydroxyl toluene and o-, p-nitro toluene give good yield of their corresponding benzoic acid. Yield was maximum with carbon as anode. The optimum conditions for the maximum yield was when the current density was  $5.67$  mA cm and the potential applied was  $0.90$  V versus SCE.

The mechanism of polymerization was postulated by studying its polarization curves. The polarization curves reveals that cathodic reduction potential of tetra methyl ammonium bromide is less negative than that of the monomer, which states that some radical mechanism is operating rather than an anodic mechanism. No polymerization take place in the absence of electrolyte. Thus the following mechanism pathway is suggested for the role of electro generated super oxide and its final utility in the formation of fuel cell for polymer synthesis.

The electron given by X is taken by oxygen to give superoxide ion.



Super oxide ion thus produced move to the fuel electrode to oxidize the carbon rod and hence conduct electricity



The electron is accepted by the monomer to give radical anion, thus finally give the desired polymer. The mechanism satisfactorily explains the increase in the rate of polymerization with increase in the concentration of electrolyte, time of electrolysis and increase in the monomer concentration.

## CONCLUSION

The present investigation provides a means to easily obtain benzoic acid derivative and than further polymerize to poly benzoic acid derivatives. Poly benzoic acid is soluble in many organic solvents and capable of being shaped into any desired form such as a film and sheet, which is considered in the prior art to be insusceptible to molding or shaping due to the insolubility there of in organic solvent by first shaping a poly benzoic acid into a film or

sheet followed by a decarbonation treatment in a suitable organic solvent while keeping the shape of polymer as such.

### **ACKNOWLEDGEMENT**

The authors are thankful to the U. G. C. for providing financial support and Principal, Govt. P. G. College Dausa (Raj) India for providing facilities for research work.

### **REFERENCES**

1. J. X. Wang, N. M. Mrkovic and R. R. Adzic *J. Phys. Chem. B.*, **108(13)**, 4127 (2004).
2. J. K. Norskow, J. Rossmeisi, A. Logadottir, L. Lindqvist, J. R. Kitchen, T. Bligaard and H. Johsson, *J. Phys. Chem. B*, **108(46)**, 17886 (2004).
3. Min-Hua Shao, Ping Liu and Radustav R. Adzic, *J. Am. Chem. Soc.*, **128(23)**, 7408 (2006).
4. Rajni Mathur and Meeta Trivedi, *Int. J. Adv. Res.*, **1(2)**, 72 (2013).
5. Meeta Trivedi and Rajni Mathur, *Int. J. Adv. Res.*, **13**, 159 (2013).
6. Rajni Mathur and Meeta Trivedi, *Acta Cinecia Indica*, **38C(4)**, 169 (2012).

*Revised : 02.05.2013*

*Accepted : 04.05.2013*