

A Novel Reaction System for Cogeneration of Chemicals and Electric Energy by Electrochemical Reduction of Nitrobenzene with Iron

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We report a novel green route for generate electric energy by simultaneously electrochemical reduction of nitrobenzene with iron which is carried out in a home-made diaphragm electrolytic cell using iron as reducer. The result shows that nitrobenzene can be reduced to aniline and its derivatives, with the main products of aniline, *p*-oxyethyl aniline and *p*-chloro aniline. During the reaction, iron will be oxidized to iron salt and simultaneously release electric energy. Effects of electrolyte, temperature, concentration of nitrobenzene, and electrodes gap on the performance of cell are studied. The corresponding open circuit cell potential is determined to be around 0.9V as the different reaction conditions. The current density varies from 1.25 to 16.25 mA cm⁻² with the change of external load. The maximum power density is 2 mW cm⁻² at 8.75 mAcm⁻². When cell's capacity reached to 1000 mAh, seven products are detected with 69% conversion of nitrobenzene and 86% of productivity at 70°C. The main products of nitrobenzene are aniline, *p*-oxyethyl aniline and *p*-chloro aniline, while iron is converted into iron ion.

Keywords: Electric energy; Cogeneration; Electrochemical reduction; Nitrobenzene; Iron

1. INTRODUCTION

Energy shortage and environmental pollution are the serious issues which human being has to face and it is urgent to explore strategies to solve the problems. People seek novel routes of primary battery for new energy source, typically, electrochemical reaction device can be reasonably used to generate electric energy and meanwhile synthesize chemicals. For example, Langer and coworkers [1-6] have reported that electrogenerative hydrogenation reactions could be preceded and meanwhile power generated and reduced organics by hydrogen. This is meaningful for production of power and compounds. In addition, much more works have been focused on this aspect, such as hydrogenation of benzene and ethylene[1-2], synthesis of H_2O_2 and oxidation of benzene[7-10], hydrogenation of unsaturated alcohols and carboxylic acid[11-12], and oxidation of glycerol[13,14], and a H_2/Cl_2 fuel cell system for production of HCl [15], a small-scale alkaline fuel cell for on-site production of HO_2^- using commercial gas-diffusion electrodes[16] a $\text{H}_2\text{-NO}$ fuel cell for the synthesis of hydroxylamine in the gas phase[17]. A certain amount of electric energy are cogenerated in these reactions aforementioned. Ma[18] also demonstrated that synthesis of cyclohexylamine and aniline with cogeneration of electrical power is possible in a fuel cell reactor by using nitrobenzene and hydrogen as reactant. The maximum power density they achieved is 1.5 mWcm^{-2} at a current density of 15 mA cm^{-2} .

The reduction of nitrobenzene is an important reaction of basic organic industrial procedure. Nitrobenzene is mainly reduced through chemical methods which are typically involved using active metal or hydrogen as reducer. Traditional industrial technology of nitrobenzene reduction by iron is often adding nitrobenzene, chloride acid aqueous solution and iron into a batch reactor. Such technologies are often not suggested because it produced a huge amount of mixture with organic wastewater and ferric oxide mud pollutant. What's more, chemical energy in oxidation-reduction reaction is not converted into usable energy[19].

Electrochemistry is an important way in development of environmental friendly organic synthesis and it is promising for reduction of nitrobenzene to produce aniline, azoxybenzene and so on [20-25]. Electrochemical dechlorination of 2,4-dichlorophenoxyacetic acid in an aqueous solution is completely converted to phenoxyacetic acid[20], the o-benzoquinone electrogenerated participates in a Michael addition reaction and the electrosynthesis of 2-(3,4-dihydroxy-phenyl)-2-methylcyclopentane-1,3-dione was carried out[21], the reduction of nitrobenzene to p -aminophenol by the preparative electrolysis with Cu and Cu(Hg) electrodes is effective and successful[22], electrochemical reduction of nitrobenzene on tungsten carbide nanocrystallines loaded onto the surface of microwave-exfoliated reduced graphene oxide (RGO) in the presence of ionic liquid (IL) has better performance[23], the converted rate of nitrobenzene of on nanoscale Fe/Au particles electrode is up to 97% and aniline was found to be the electrolysis product[24], the electrochemical reduction of nitrobenzene over Cu/MWCNT in acidic ethanolic medium with an overall selectivity toward azoxybenzene (AOB) of 82%[25]. These reaction has good effectiveness and is environmental friendly process, but these process must consume electricity to produce relative products.

In this study, a novel reaction system for generation of electric energy by electrochemical reduction of nitrobenzene with iron is proposed. A home-made diaphragm electrolytic cell was

developed as reactor, in which NB and iron were put in different chamber which were separated by anion exchange membrane, both the anode and cathode chamber can obtain useful chemicals: aniline, *p*-oxyethyl aniline and *p*-chloro aniline were main products in cathode chamber, while iron salt is anode product. There is no trouble for separating the mixtures of iron oxides and organic compounds and made it easy for separation of products, and thus pollution is greatly reduced. Meanwhile a certain amount of electric energy is cogenerated. It is an environment-friendly novel route to produce energy and usable chemicals.

2. EXPERIMENTAL

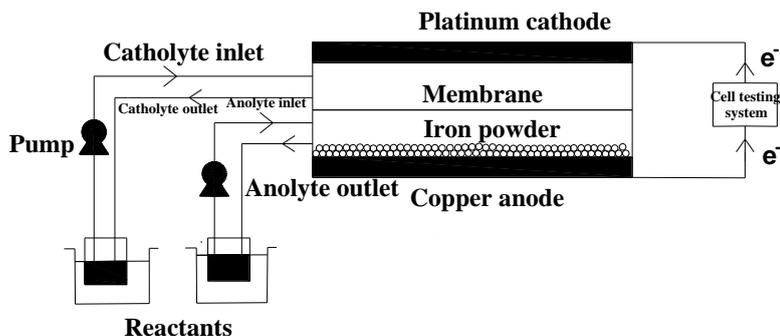
All the chemicals were of analytical grade and used without further purification. All the aqueous solutions were prepared with ultra pure water.

A home-made electrolytic cell which consisted of copper electrode in the anode chamber, platinum electrode in the cathode chamber, and equipped anion exchange membrane as the diaphragm was used for this study. Platinum cathode(2×2 cm, purchased from Wuxi international platinum Co.Ltd.) was pretreated by polishing with sandpaper, and then cleaned ultrasonically with acetone, dilute nitric acid, and deionized water, respectively. Cu anode was treated as the same method as that for Pt cathode. The diaphragm was anion exchange membrane (3368 heterogeneous ion exchange membrane, Shanghai Shanghua Water Treatment Material Co.,Ltd). The electrode for the cathode contained nitrobenzene, ethanol and hydrochloric acid. Two kinds of anolyte were used, 0.25 mol L⁻¹ ammonia sulfate aqueous solution and 0.5 mol L⁻¹ ammonia chloride aqueous solution, respectively. The procedures for chemical reaction and generation electric power were carried out in a cell reactor system illustrated by Scheme 1. When external circuit is closed, electrons attributed to Iron are transferred from anode through external circuit to cathode and obtained by nitrobenzene, electron current is achieved respectively. In the meantime, in internal cell, chloride ions in cathode chamber are migrated to anode via anion exchange membrane, and ion current is formed. There are many kinds of chemicals in cathode chamber, such as aniline, azoxybenzene, etc. Fe²⁺ are produced in anode chamber.

The cathode solution and the anode solution was transferred by pumps and the flow rate of the solution is 63mL/min. Cell performance was tested by Wuhan Land battery testing system.

The catholyte in which nitrobenzene was reduced under constant current density was firstly distilled to remove ethanol, and then the products in residual solution were extracted with methylbenzene.

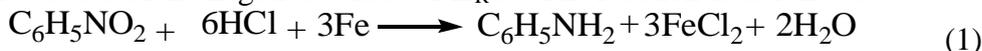
The concentration of reactants and products were identified by GC/MS method using TRACE DSQ GC/MS equipped with capillary column(TR-5MS, 30m × 0.25mm × 0.25μm). The conversion of nitrobenzene and selectivity to the individual product was similar to the equations described elsewhere [18].



Scheme 1. Schematic configuration of the experimental apparatus.

3. RESULTS AND DISCUSSION

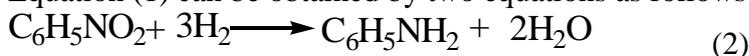
Generation of power by the electrochemical reduction of nitrobenzene has been successfully carried out in an electrochemical device. Reduction of nitrobenzene occurs spontaneously with iron as reducer because of the negative values of $\Delta_R G^\theta$. The reaction is as follows:



According to $\Delta_R G^\theta = -nFE^\theta$, the E^θ of the reaction can be calculated out, where

$\Delta_R G^\theta$ is free energy change which calculated by the standard free enthalpy change according to the overall chemical reaction, E^θ is electromotive force, n is the number of transport electrons and F is the Faraday constant of 96500 coulombs. From Langer’s summary [3], $\Delta_R G^\theta$ of hydrogenation of nitrobenzene is $-122.4 \text{ kcal mol}^{-1}$.

Equation (1) can be obtained by two equations as follows:



So the $\Delta_R G^\theta$ of reduction of nitrobenzene by iron can be calculated according to:

$$\Delta_R G^\theta = -122.4 \text{ kcal mol}^{-1} + \sum v_i(\Delta_F G^\theta) \quad (4)$$

Where v_i is the stoichiometric factors of each reactant in equation (3), $\Delta_F G^\theta$ is values of standard free enthalpy of formation of the reactants in equation (3). And E^θ of equation (1) is calculated to be 1.29V [26]. But open circuit voltage determined in experiment is around 0.9V with reaction condition: 0.5 mol L^{-1} ammonia chloride aqueous solution, 70°C , 0.5 M nitrobenzene, 1cm of electrodes gap, which is lower than 1.29 V, because the anolyte used is difference from equation(1), and $\Delta_R G^\theta$ is in standard state, which is different from the state used in experiment.

3.1 The discharge performance of cell

Fig.1 shows the discharge performance of the cell using various anolyte. It is found that when 0.5 mol L^{-1} ammonium chloride aqueous solution is used as anolyte, the discharge voltage and the

discharge power density of the cell is higher than that used 0.25 mol L⁻¹ ammonia sulfate aqueous solution. And when 0.5 mol L⁻¹ ammonium chloride aqueous solution is used as the anolyte, the maximum power density is 2 mW cm⁻², which is higher than 0.25 mol L⁻¹ ammonia sulfate aqueous solution. And it is higher than 1.5 mWcm⁻² in Ma's work at 70°C[18]. In Ma's work nitrobenzene is reduced with hydrogen gas and electric energy is cogenerated. The oxidation of hydrogen is a heterogeneous reaction on electrode surface, the reaction rate is slower than the oxidation of iron powder in electrolyte solution. And the pressure of hydrogen gas is limited in a certain range, but the effective concentration of iron powder can be easily increased through increasing the amount and reducing the particle size of the powder. Therefore this reaction system is more advantageous in generating electricity than Ma's work[18]. What's more, different anolyte can be chosen for different requirements. For example, 0.5 mol L⁻¹ ammonium chloride aqueous solution can be chosen for preparation of iron dichloride, and 0.25 mol L⁻¹ ammonia sulfate aqueous solution can be chosen for ferrous sulfate. In what follows, 0.5 mol L⁻¹ ammonium chloride aqueous solution is used as anolyte.

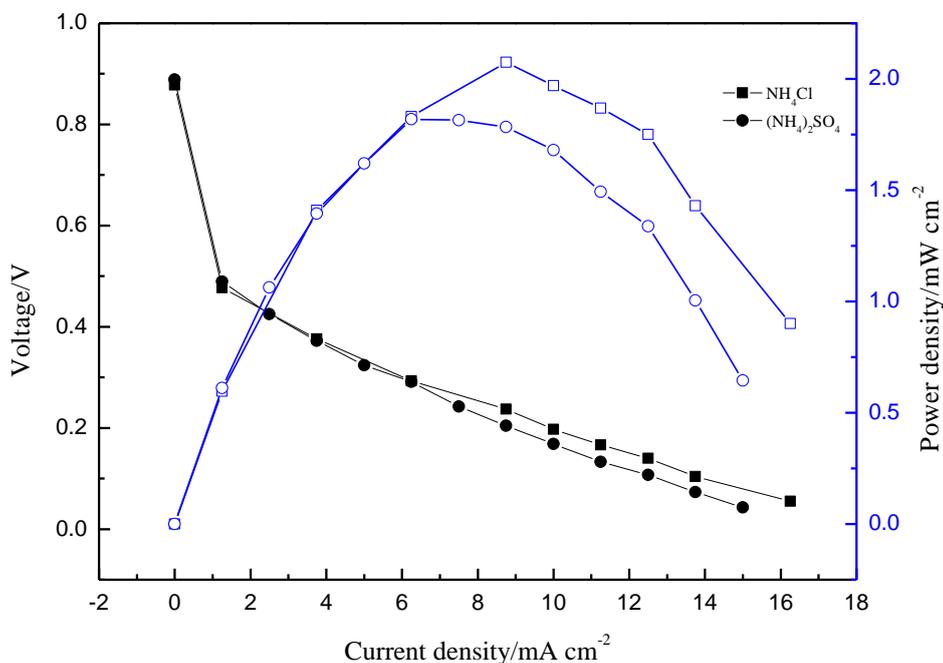


Figure 1. Cell performance at 70°C with different anolyte with different anolyte.

Influence of temperature on discharge performance of the cell is investigated on following condition: concentration of nitrobenzene is 0.5 mol L⁻¹, anolyte is 0.5 mol L⁻¹ ammonium chloride, and the flow rate of anolyte and catholyte is 63 mL/min. It can be seen from Fig.2, with the increase of temperature, the cell voltage and the power density of the cell is increased at the same current density. With current density changed from 1.25 to 16.25 mA cm⁻², it is found that at each temperature, the voltage of the cell is lower at high current density than that at low current density. The power density of the cell increases when the current density is lower than a certain value, and the power density of cell decreases when the current density is higher than a certain value. A maximum power density can

be found that it is 2 mWcm^{-2} at 8.75 mAcm^{-2} at 70°C , which is higher than 1.5 mWcm^{-2} at 15 mAcm^{-2} in Ma's work[18] and in Otsuka's work[8]. So the optimal experimental temperature is 70°C .

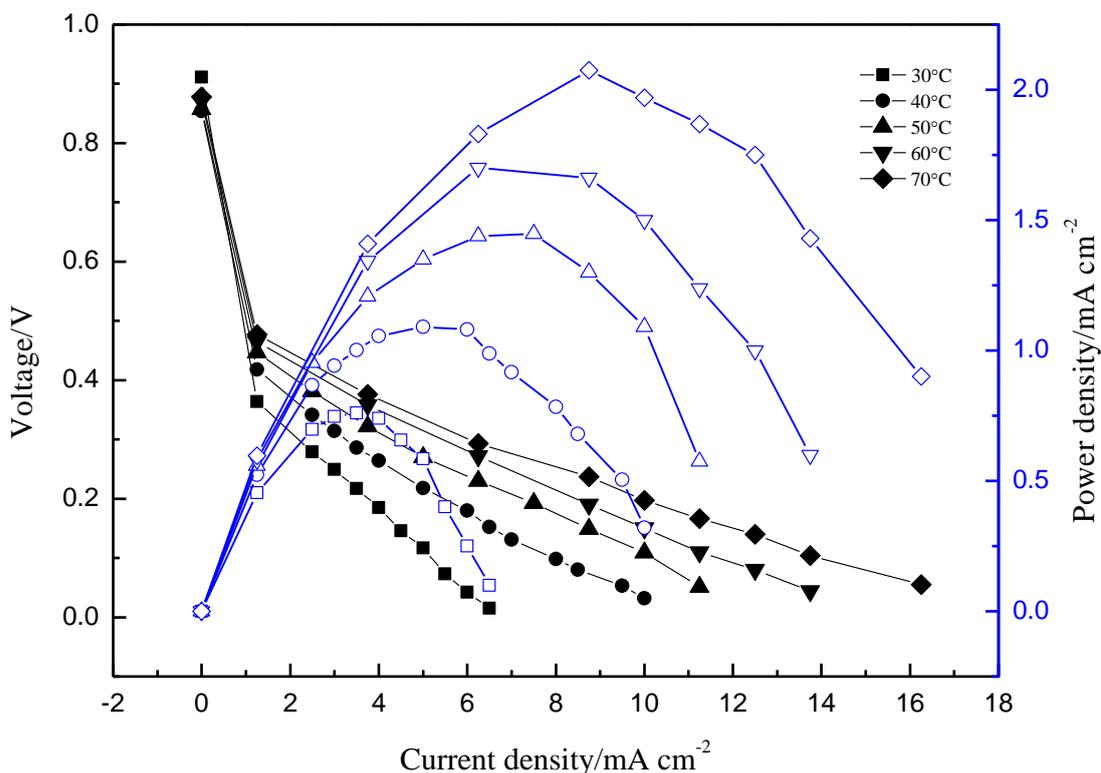


Figure 2. Cell performance at different temperatures.

Fig.3 shows cell performance in different concentration of nitrobenzene at 70°C . It indicates that the maximum current density increases from 6.5 mA cm^{-2} to 16.25 mA cm^{-2} with increase of nitrobenzene concentration from 0.1 to 0.5 mol L^{-1} . The voltage of discharge increases with increasing of concentration of nitrobenzene at the same current density. It is clear that the higher concentration of nitrobenzene results in the higher cell performance. As the concentration of nitrobenzene increases, the concentration polarization current density, the discharge voltage and the power density increase.

Fig.4 shows the influence of electrodes gap on cell performance. It can be seen that, the discharge voltage and voltage and power density of cell with 1 cm electrode gap is higher than that with 2 cm electrodes gap at the same current density. And when the gap is 1 cm , the maximum power density is 2 mWcm^{-2} , while the gap is 2 cm , the maximum power density is 1.4 mWcm^{-2} , which is due to decreasing electrode gap can reduce the internal resistance of cell.

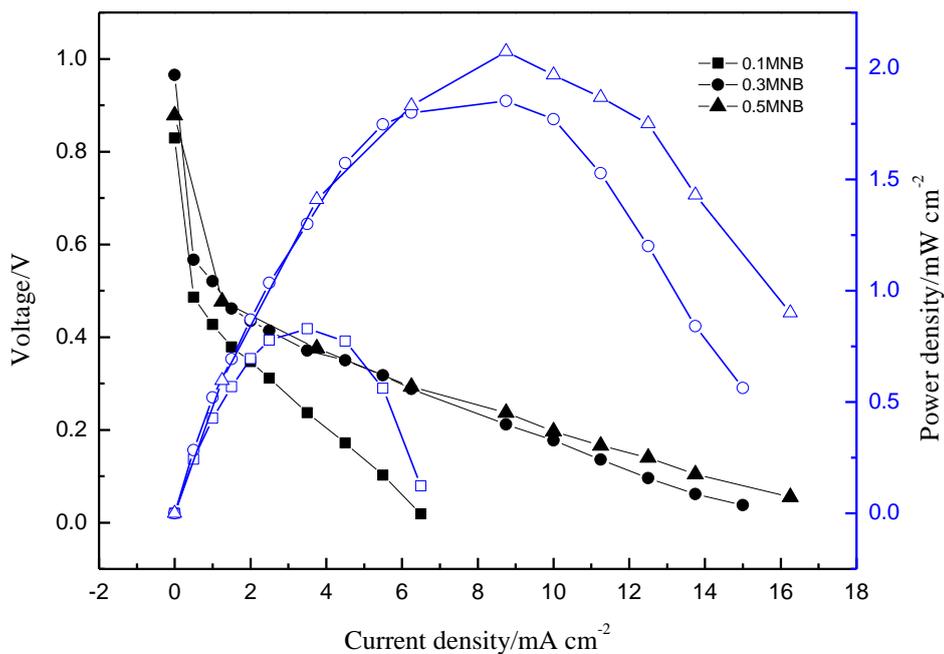


Figure 3. Cell performance at 70°C with different concentration of NB. Anolyte consists of 0.5 mol L⁻¹ ammonium chloride. Flow rate of anolyte and catholyte was 63mL min⁻¹. Electrode gap was 1 cm.

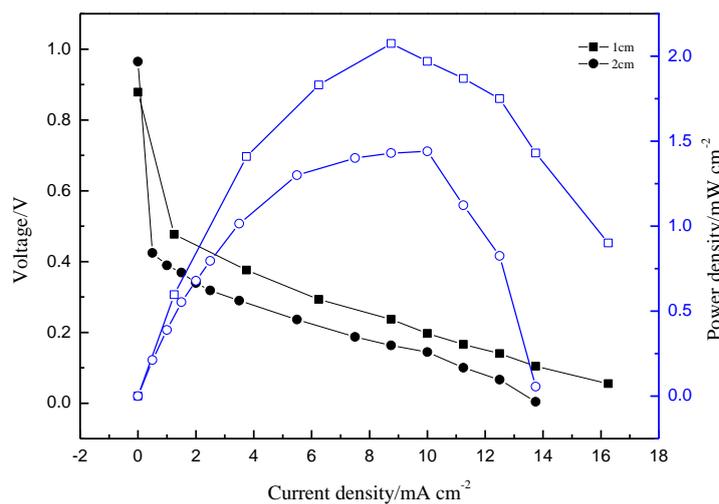


Figure 4. Cell performance at 70°C with different electrode gap. Catholyte was 0.5mol/L NB+3.5mol/L HCl solved in ethanol. Anolyte was 0.5 mol L⁻¹ ammonium chloride. Flow rate of anolyte and catholyte was 63mL/min.

3.2 The synthesis performance of the cell

Products are qualitatively analyzed by GC/MS. There are eight chromatographic peaks can be seen in Fig.5 and Table 1 shows the retention time and corresponding materials, besides nitrobenzene,

aniline and the derivatives of aniline and azoxybenzene are produced by reducing nitrobenzene in discharge reaction.

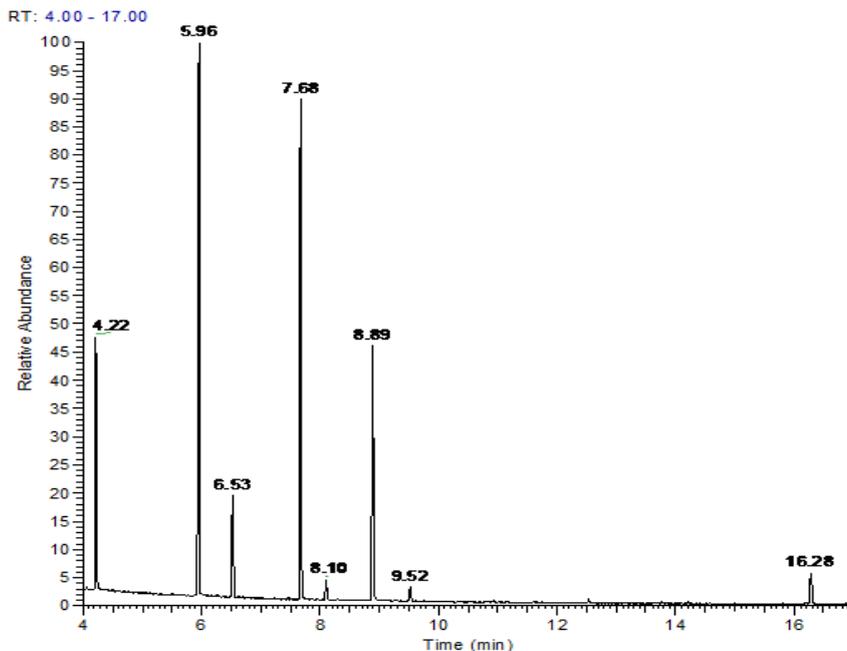


Figure 5. Chromatogram of products.

Table 1. Retention time and corresponding products.

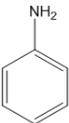
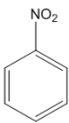
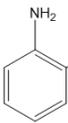
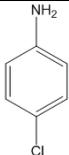
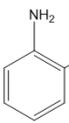
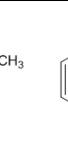
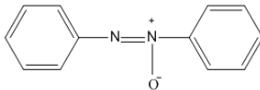
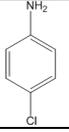
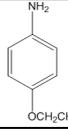
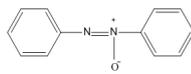
Retention time/min	4.22	5.96	6.53	7.68	8.10	8.89	9.52	16.28
Chemicals								

Table 2. Conversion of NB, product yield and selectivity of seven kinds of products.

Conversion of NB(%)	Selectivity(%)							Product yield(%)
								
69	22.24	6.99	37.71	1.18	16.67	0.71	0.92	86

Catholyte was 0.5mol/L NB+3.5mol/L HCl solved in ethanol. Anolyte is 0.5 mol L⁻¹ ammonium chloride. Flow rate of anolyte and catholyte was 63mL/min. Cell's discharge capacity was 1000 mAh.

These chemicals are important materials in industry. The analysis result of sample is showed in Table 2. When cell's discharge capacity reached to 1000 mA h, the conversion of NB is 69% and total productivity is 86%. And the current efficiency is 87%. The main products are para-chloroaniline, aniline and para-oxyethylaniline, respectively.

4. CONCLUSION

In summary, as a new of power source electrochemical reduction of nitrobenzene by iron can be carried out in the home-made diaphragm electrolytic cell. Typically, the reaction within the home-made diaphragm electrolytic cell undergo iron electro-oxidation and nitrobenzene electro-reduction hydrogenation. The discharge performance of the cell is affected by the type of electrolytes, temperature, concentration of nitrobenzene, and electrodes gap. The main products of cathode chamber are para-chloroaniline, aniline and para-oxyethylaniline respectively, while iron salt is the product of anode chamber. This method is green and environment-friendly, the current density and power density is also higher than using hydrogen as reducer.

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