

# Electrochemical Oxidation of Phenol using a Flow-through Micro-porous Lead Dioxide/Lead Cell

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## ABSTRACT

The electrochemical oxidation of phenol to benzoquinone followed by the reduction to hydroquinone and catechol was demonstrated by constructing a three-dimensional porous micro-flow cell from lead dioxide and lead. The electrodes were made by using the principles of curing and formation of lead oxide material that are common in the construction of the electrodes used in lead-acid batteries. This resulted in highly porous electrodes that can allow the reactant solution to flow through them in series, without the risk of having the products being oxidized again at the anode that usually occurs in a simple undivided cell. In this study, a 50 mM solution of phenol in a 60 % acetonitrile and water mixture was used that contained 2 % sulphuric acid. The reactant solution would flow through the anode porous material oxidizing the phenol to benzoquinone. The benzoquinone in solution would then flow through the cathode porous material and reduce to catechol and hydroquinone. The study showed that almost all of the phenol could be converted in one continuous flow process in using a relatively low cost electrochemical micro-flow cell that can be easily scaled up to accommodate larger volumes and concentrations by using electrode manufacturing principles used in the lead-acid battery industry.

## KEYWORDS

Phenol, hydroquinone, catechol, lead dioxide, micro-flow cell.

## 1. Introduction

The electrochemical oxidation of phenol is described in the literature in terms of converting phenol or similarly structured organic chemicals to a variety of products ranging from organic acids to hydroquinone and catechol and also to carbon dioxide.<sup>1-4</sup> The synthesized hydroquinone and catechol are important starting materials for further synthesis of pharmaceuticals, food flavourings and anti-oxidants.<sup>5</sup> Other studies done on the oxidation of phenol include techniques such as photolysis and bio-catalysis,<sup>5,6</sup> and the use of micro-structured catalytic wall reactors.<sup>7</sup>

The mechanism of anodic oxidation of phenol to benzoquinone<sup>8,10</sup> and its further reduction to hydroquinone are well known.<sup>9,11,13</sup> Electrode materials are proposed that can range from Pt, graphite and Ni to PbO<sub>2</sub>, where PbO<sub>2</sub> was shown to be useful in the electro-catalytic oxidation of phenols and nitrophenols.<sup>4,6</sup> PbO<sub>2</sub> is well suited as electrode material due to its stability in a corrosive aqueous environment, combined with its high conductivity, relatively low cost and ease of manufacturing. It also has a relatively high oxygen evolution potential when compared to other metals such as Pt. PbO<sub>2</sub> is also one of the main components used in the Pb-acid battery industry where it can be subjected to a large number of electrochemical discharge and charge cycles.<sup>15,16</sup>

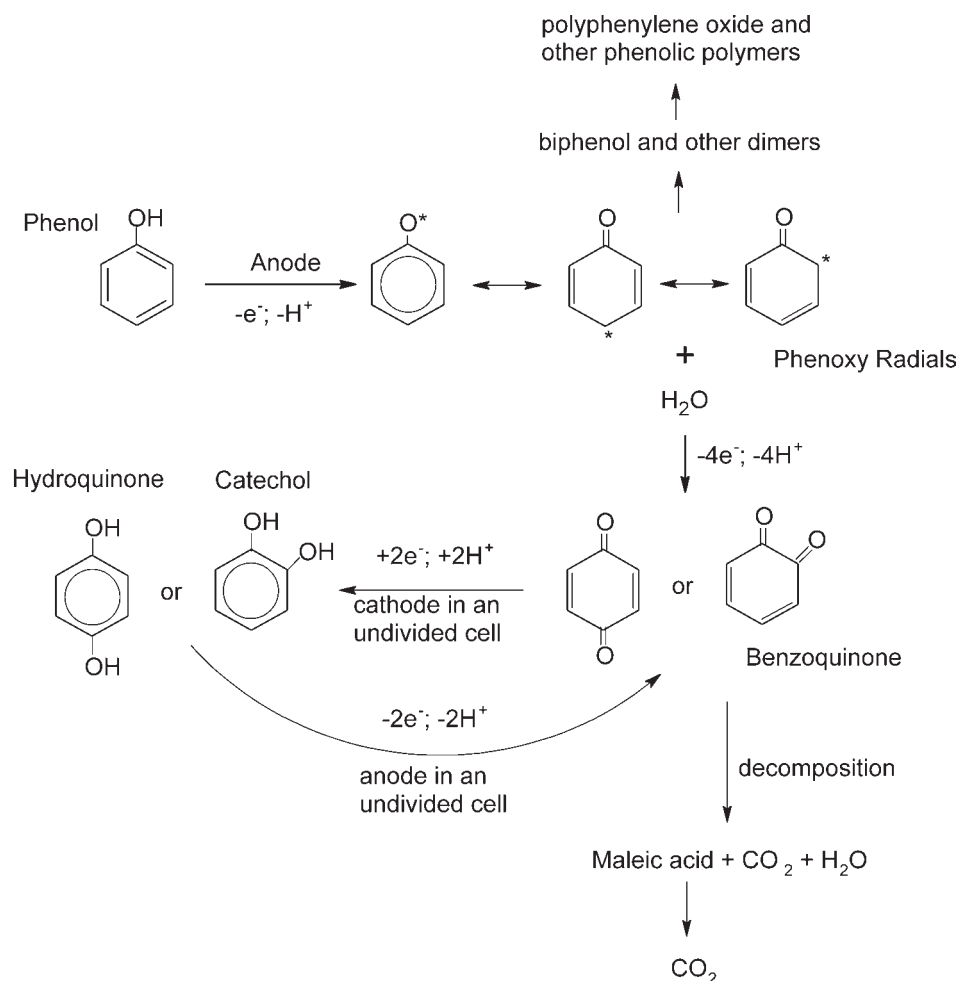
However, the use of phenol in a plain acidic aqueous electrochemical cell can quickly passivate the PbO<sub>2</sub> electrode surface. The resulting layer occurs due to the electro-polymerization of phenol that can act as a protective coating for the electrode surface thereby preventing further contact with the electrolyte solution.<sup>11</sup> Acetonitrile was shown to be a suitable co-solvent

with water in reducing the effect of the passivation of the electrode surface.<sup>4,11</sup>

The oxidation and reduction mechanisms of phenol to its various products in a typical electrochemical cell are shown in Fig. 1.<sup>8,11,13</sup> The phenol is oxidized on the PbO<sub>2</sub> anode to produce the phenoxy radical. In the presence of water, the reaction can proceed further to form the *o*- or *p*-benzoquinone. However, if a sufficient amount of the phenoxy radicals is present, dimers and even larger phenolic polymers such as polyphenylene oxide can form. This was described as the main contributor to the passivation of the electrode. Under certain conditions and with other solvents present, such as acetonitrile, the polymer formation can be limited and the formation of benzoquinone is encouraged.<sup>4</sup> The benzoquinone would then reduce at the cathode to the desired products, predominantly hydroquinone and catechol. However, in a stirred solution within a typical undivided cell, the hydroquinone would easily oxidize back to the benzoquinone at the anode, thereby reducing the formation of the desired hydroquinone. Some authors have described the use of a divided cell to form the benzoquinone in the anode compartment, after which the benzoquinone solution is transferred to the cathode department for reduction to the final product of hydroquinone and catechol.<sup>14</sup>

Most organic electrochemical synthesis reaction occur within a simple three-electrode batch cell, where the electrode configuration is made up of a working, counter and reference electrode. There are some systems that are described in terms of a flow-through micro-reactor for typical applications such as the organic waste treatment of water where the porous anode and cathode are in the same direction as the flow of the aqueous solutions.<sup>1-3</sup> In this case, the description of the cathode and

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**Figure 1** The reaction mechanism of phenol in an aqueous solution within an electrochemical cell.<sup>4,7,9</sup>

anode materials can be relatively complex with electrodes having large pore volumes with low surface areas. These systems might be well-suited for the complete decomposition reaction of waste phenol to  $CO_2$ , but not for the controlled reaction of phenol to the intermediates of hydroquinone and catechol, when the applied cell potential has to be set within certain controlled values. Literature has reported that the rate of the oxidation of phenol at the anode can be considered as the rate-limiting step with low conversions of up to 50 % to the desired reaction product.<sup>7,14</sup> For such a flow-through cell, high surface area with narrow flow-through capillaries of the anode would be desired to allow sufficient contact time with the reacting species.

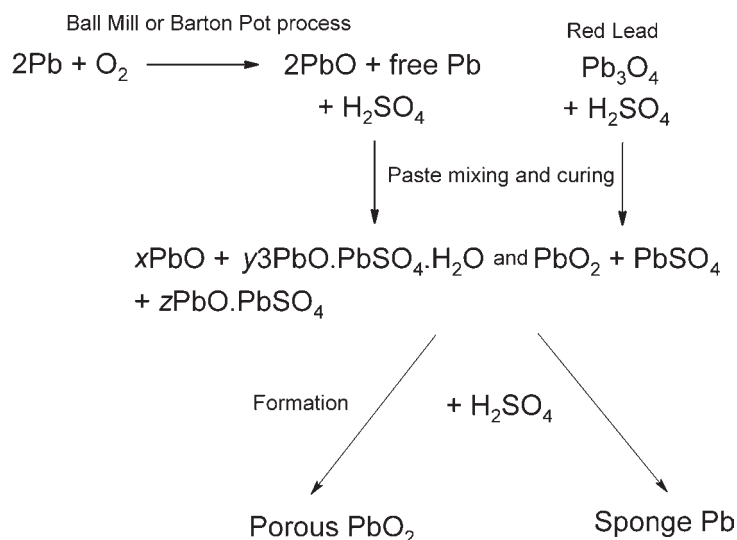
In the manufacturing of the positive electrode within a Pb-acid battery, PbO or a mixture of PbO and  $Pb_3O_4$  (red lead) are used in conjunction with sulphuric acid to make a cured active material of mainly monobasic and tribasic lead sulphate. The cured active material is then subsequently 'formed' in sulphuric acid to make the  $PbO_2$  and Pb electrodes respectively. The initial red lead is used to improve the formation process of the cured material, since it forms  $PbO_2$  on reacting with sulphuric acid during the paste mixing. The small amounts of conductive  $PbO_2$  in the presence of non-conducting cured active material allows for easier and complete formation to the final  $PbO_2$  active material. These processes are used for both the manufacturing of the flat plate automotive type and the industrial tubular electrode either by dry oxide or paste filling processes.<sup>15,16</sup> The cured active material forms a hard three-dimensional structure that gives shape to the active material and maintains the plate's integrity

during the formation process. The cured active material, that can contain a range of lead oxide sulphates, has a relatively large surface area and a porosity that consist of many micro-channels. During formation, this is converted to the desired porous  $PbO_2$  as the positive electrode or 'sponge' Pb as the negative electrode that allows the acid electrolyte to penetrate relatively deeply into the active material for optimum utilization (Fig. 2).

In this study, the concept of making a positive  $PbO_2$  electrode with micro-channels with a relatively large surface area was combined with the idea of a continuous flow-through cell where a more accurate control of the cell potential can be obtained to synthesize the desired quinone products by using a solution containing phenol as the starting material. The cell was constructed in such a way that a continuous feed of an aqueous acetonitrile solution containing phenol flowed through the three-dimensional micro-channel electrodes whilst the cell's potential and reactant flow rate was easily controlled. This allowed the entire phenol content in the solution to be converted to the desired product in a continuous process.

## 2. Experimental

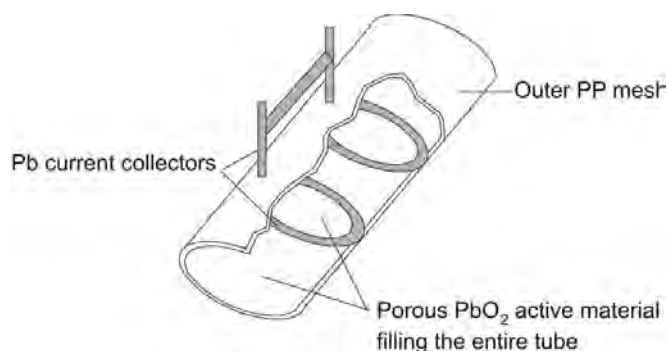
Some initial studies on the behaviour of the positive ( $PbO_2$ ) and negative (Pb) electrodes in phenol-containing solutions were performed by cyclic voltammetry on a BAS CV50 potentiostat. A pure Pb electrode with a diameter of 5 mm was embedded in resin and polished. In the cell, to investigate the effects on the  $PbO_2$ , the surface of the polished Pb electrode was oxidized by maintaining it at a potential of 1500 mV *vs.*



**Figure 2** Simple flow diagram illustrating the manufacturing process of the active material used in lead-acid battery electrodes.

Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode for 2 min before commencing with the scanning. The various concentrations of phenol in the aqueous/acetonitrile were studied and the behaviour of both the positive and negative electrode reported. This was done in order to confirm the findings of the literature on the effect of polymeric phenol passivation and to determine the suitable potential windows for the oxidation of phenol in the particular solution mixtures using a K<sub>2</sub>SO<sub>4</sub> saturated Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode.<sup>4</sup> A Hg/Hg<sub>2</sub>SO<sub>4</sub> reference was used in order to avoid possible contamination (Cl<sup>-</sup> ions) since the reference electrode remained in the cell for the duration of the experiments. The scan rate used was 10 mV s<sup>-1</sup> between -1800 mV and 1800 mV *vs.* the Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode.

The flow-through anode was constructed by using a meshed polypropylene cylinder (20 mm diameter and 40 mm in length). Disc-shaped current collectors made from Pb sheets were inserted into the polypropylene housing ensuring that sufficient space was allowed for the filling of the active material (Fig. 3). An initial meshed polypropylene cylinder was used to allow for the sulphuric acid to flow around the cured active material in order to ensure that complete formation occurred for the entire electrode bulk material. The tube was initially filled with a powder mixture of PbO (Barton Pot oxide) and 20 % by mass Pb<sub>3</sub>O<sub>4</sub>. The oxide contained about 20 % free Pb and had a final dry packing density of 4.0 g cm<sup>-3</sup>. The cell was allowed to 'pickle' in 1.1 SG sulphuric acid for about half an hour before the cell with its active material was cured at 30 °C for 48 h. After curing the electrode, it was formed in an electrochemical cell containing a formation acid of 1.15 SG with two corresponding cured nega-



**Figure 3** A meshed polypropylene cylinder filled with porous PbO<sub>2</sub> and Pb disc-shaped current collectors.

tive electrodes situated on both sides of the cylindrical positive electrode.

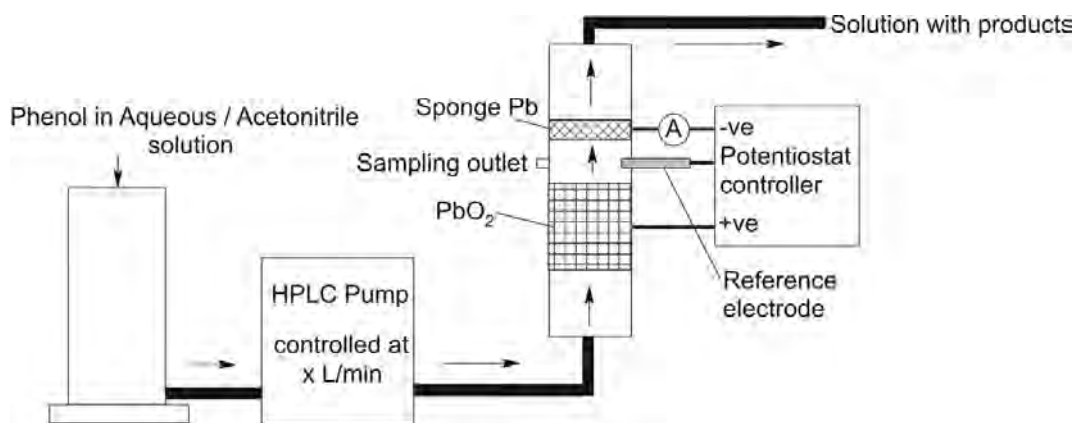
The initial formation current was kept relatively low (0.5 A) and increased in a step-wise fashion until the entire electrode was formed within about three days. Duplicate electrodes in series were also formed and used for further analysis by X-ray powder diffraction to ensure complete PbO<sub>2</sub> formation of the active material in the cell. The X-ray diffraction analysis was done using Bragg Brentano geometry on a Bruker D8 powder diffractometer using Cu radiation. A Ni filter was used at the detector and the scan range was from 5 to 60 2θ at 0.02 deg step<sup>-1</sup>. The duplicate electrodes were also further analyzed for their BET surface area by nitrogen adsorption on a Micromeritics Gemini III 2375 analyzer and their porosity by Hg porosimetry on a Micromeritics Autopore II 9215.

Suitable sections from a 5 mm thick negative pasted manufactured battery plate used in typical flat plate industrial Pb-acid batteries were used for the formation of the sponge Pb electrode.

The cylindrically formed PbO<sub>2</sub> anode was then further assembled into a larger solid polypropylene cell housing ensuring that the Pb current collectors protruded for their connection to an external power supply. Care was taken to ensure that no electrolyte would be able to flow around the outer edges of the cell assembly and that it would be kept within the length of the porous active material.

Similarly, two of the 5 mm thick sections of the porous sponge Pb cathode were moulded in series with the anode into the cylindrical polypropylene cell housing allowing sufficient lengths of the current collector to protrude for connections to a potentiostat. The cell was connected in series with a suitable HPLC pump that allowed careful control of the flow of solutions containing the starting material (Fig. 4). A sampling outlet with a plastic tap and an Hg/HgSO<sub>4</sub> reference electrode were inserted in the section between the two electrodes. The sampling outlet was used at regular intervals during the experiment to determine the intermediate products formed between the two electrodes and the reference electrode was used to control the applied potential *vs.* the working electrode.

Suitable amounts of sample were taken from the product stream at regular time intervals and analyzed on a Hewlett Packard 1100 series HPLC with a dual pump system equipped with a variable UV-Vis detector and an autosampler unit. The chromatographic separation was done using a Waters micro



**Figure 4** A flow diagram describing the construction of the flow-through electrochemical cell using micro-porous  $\text{PbO}_2$  and  $\text{Pb}$ , respectively, for the conversion of phenol to hydroquinone and catechol.

Bondpak  $\text{C}_{18}$  column where the mobile phase was a pH 3 buffered water:methanol mixture (80:20 v/v) and the detector was set at 280 nm where the resulting peak areas were integrated using the HP Chemstation LC software. Analytical grade standards of the starting material (phenol) and the expected main products (hydroquinone, catechol, benzoquinone and 4,4 biphenol) were obtained and a suitable calibration of the HPLC technique for each was done by the preparation of accurate standard solutions by considering the changes in the eluted HPLC peak areas with change in solution concentration.

The flow-through cell was controlled by an HPLC pump where the flow rates for the duration of the experiments were kept at  $0.5 \text{ cm}^3 \text{ min}^{-1}$ . A range of acetonitrile/water solutions with 2 %  $\text{H}_2\text{SO}_4$  was initially tried out and optimized by CV studies to be 60/40 (v/v); this mixture was then used for the duration of the flow-through cell experiments. The starting concentration of phenol chosen for this study was kept at 50 mM. Higher concentrations of phenol solutions were investigated and were shown not to be suitable for the size of cell design considered in this study. The flow-through cell was initially flushed with the acetonitrile/water acid solution containing no phenol for about  $\frac{1}{2}$  hr where the potential across the cell was set to 3.2 V and allowed to stabilize. This was followed by the 50 mM solution of phenol and sufficient solution was allowed to flow through the

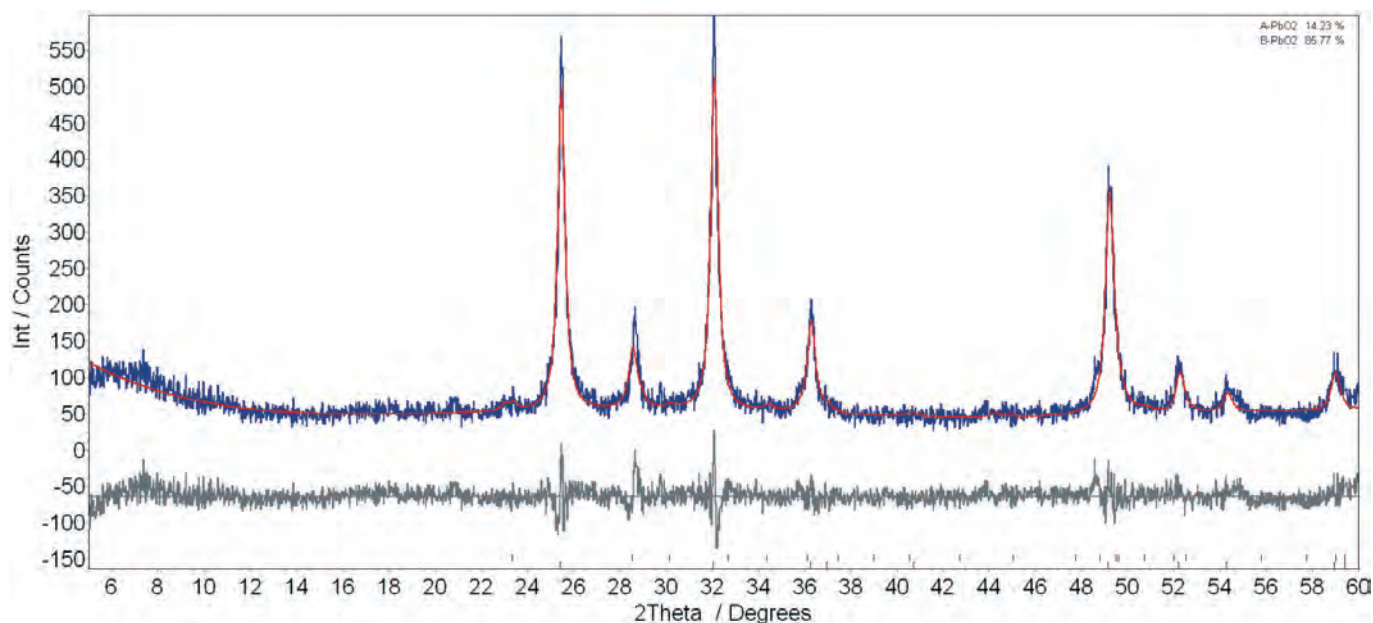
cell before sampling commenced. An aliquot sample of 0.5 mL was taken at regular time intervals, diluted with 2 mL of methanol for HPLC analysis. All experiments were done at room temperature and the variations in cell potential, the potential *vs.* the  $\text{Hg}/\text{Hg}_2\text{SO}_4$  and the current flow were recorded using a suitable data logger.

### 3. Results and Discussion

#### 3.1. Surface Analysis and Characterization of the $\text{PbO}_2$ Anode Material

The PXRD analysis and quantification of the solid phase composition of the cylindrical flow-through anode by Rietveld refinement using Topas<sup>®</sup> showed that the active material contained predominantly  $\beta\text{-PbO}_2$  with about 14 %  $\alpha\text{-PbO}_2$  and that complete formation of the active material had occurred since there was no residual  $\text{PbSO}_4$  present (Fig. 5). The beta phase of the  $\text{PbO}_2$  would be more favourable for the oxidation of the phenol.<sup>4</sup>

The BET surface area of the formed active material for the anode was  $2.71 \text{ m}^2 \text{ g}^{-1}$ . The micropore volume distribution that was measured by Hg porosimetry showed it to have a porosity of 51.57 % with a median pore diameter of  $0.651 \mu\text{m}$  (Fig. 6). The apparent and bulk densities as measured by Hg porosimetry



**Figure 5** PXRD diffraction pattern of the anode material showing the quantification of its phase composition using Topas Rietveld refinement.

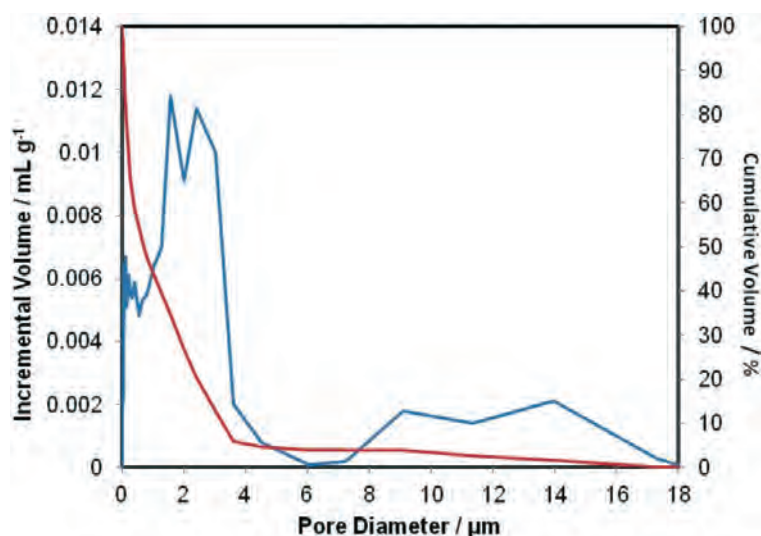


Figure 6 The micropore volume distribution as measured by Hg porosimetry of the anode active material.

were  $7.26 \text{ g cm}^{-3}$  and  $3.51 \text{ g cm}^{-3}$ , respectively, with an intrusion volume of  $0.147 \text{ cm}^3 \text{ g}^{-1}$ .

The surface area to volume ratio (SA:V) is an important parameter of solid materials for catalysts that are used in chemical reactions. It is a parameter commonly used in micro-reactor systems and can be an indication of the possible efficiency at which a reaction could proceed. Typical micro-reactors are reported to have a ratio of 100 to  $200 \text{ cm}^{-1}$  when compared to a conventional batch-type reaction that was done in a 100 mL flask where the ratio could be between 0.06 to  $1 \text{ cm}^{-1}$ .<sup>17</sup> The main advantages of micro-reactor systems are their high SA:V ratio that would allow for careful temperature control of highly exothermic systems and effective mixing. In this particular system under study, heat transfer was not a problem, but there was a need for good mixing and effective contact of the reagent (in this case phenol) with the electrode surface to allow for the relatively slow kinetic electro-reaction to take place.

Using the surface area that was determined by BET nitrogen adsorption analysis and the porosity that was determined by Hg porosimetry, the SA:V can be calculated by considering the  $\text{PbO}_2$  cylindrical electrode (2.0 cm diameter by 4.0 cm in length) with a volume of approximately  $12.57 \text{ cm}^3$  and an active mass of 39.55 g (excluding the current collectors). With a porosity of 51.57 %, the porous volume of the active material would be  $0.1639 \text{ cm}^3 \text{ g}^{-1}$  and hence, the SA:V for the electrode material would then be  $165\,342 \text{ cm}^{-1}$ . One could also consider the intrusion volume that was determined by Hg porosimetry of  $0.1471 \text{ cm}^3 \text{ g}^{-1}$  and the BET surface area, then a SA:V of  $184\,228 \text{ cm}^{-1}$  would be calculated. Either way, this showed that the two methods of calculating the effective SA:V resulted in values that are larger by a significant order of magnitude than conventional micro-flow systems which report values of up to  $200 \text{ cm}^{-1}$ .<sup>17</sup> The large ratio determined for the  $\text{PbO}_2$  electrode was due to the three-dimensional micro-porous structure of the active material that can act as useful sites for the electro reaction to take place. The resulting cylindrical  $\text{PbO}_2$  electrode was porous enough to give minimal back pressure from the solution flow and to provide a sufficiently high surface area for the conversion of the phenol to the desired benzoquinone, which would then be reduced to the hydroquinone/catechol at the Pb cathode.

The cathode (Pb) was made from thin plate electrodes that are used in the manufacturing of automotive starting, lighting and ignition (SLI) batteries where the porosity of the active material could typically vary between 51 % and 65 %.<sup>18</sup> This porosity

would be sufficient to allow the reactant solution to flow through the three-dimensional sponge Pb structure allowing for the easy reduction of the benzoquinone to desired hydroquinone.

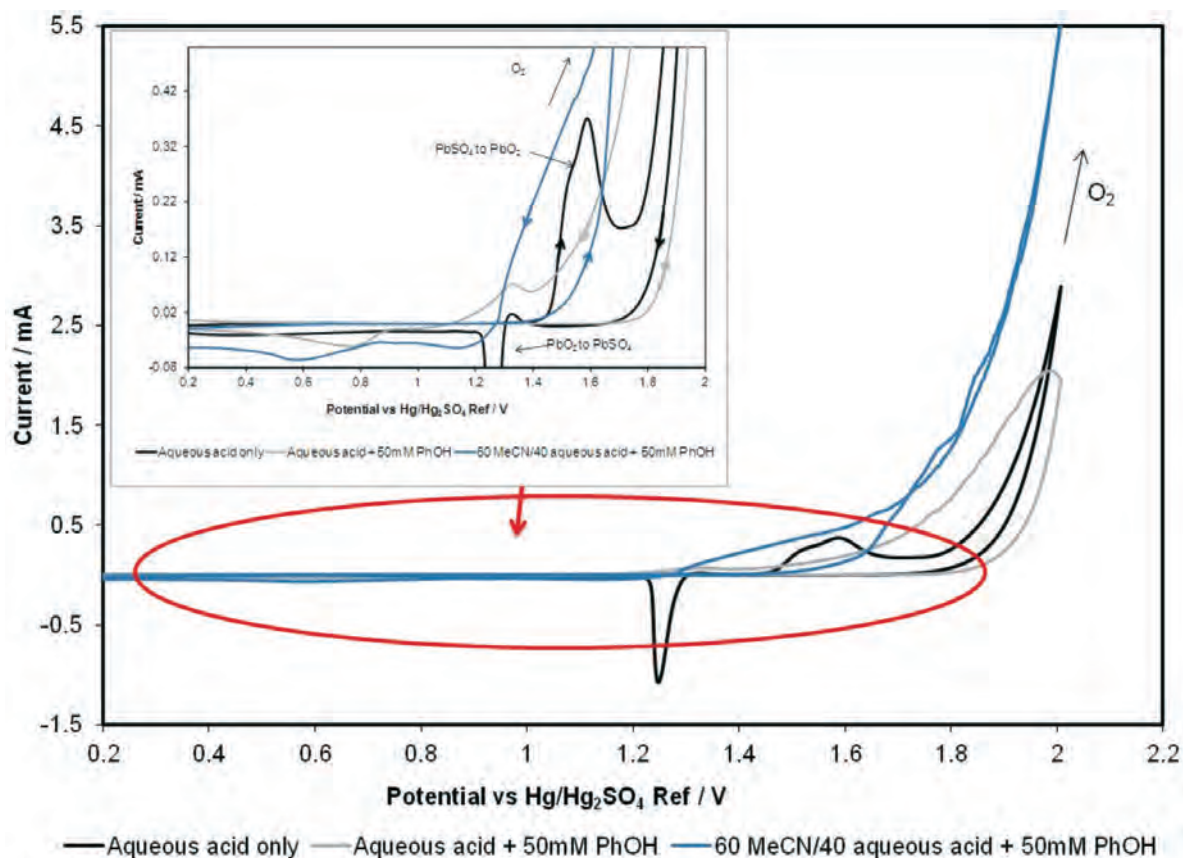
### 3.2. Electrochemical and Micro-flow Cell Studies

The cyclic voltammograms (CV) of the  $\text{PbO}_2$  electrode vs. the Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode in a 2 % H<sub>2</sub>SO<sub>4</sub> aqueous solution with and without 50 mM phenol are shown in Fig. 7. The results showed that in the acid solution alone, the typical reversible oxidation and reduction reactions can be seen that are associated with  $\text{PbO}_2$  and  $\text{PbSO}_4$  respectively. In the aqueous acid solution containing phenol however, the electrode surface would quickly become passivated in the forward positive scan direction as illustrated by the decrease in the  $\text{PbSO}_4$  to  $\text{PbO}_2$  that occurred around 1.35 V shown in the magnified insert in Fig. 7. However, in the reverse scan direction, a small oxidation peak near 1.35 V was observed followed by a reduction peak near 0.8 V. These peaks could be ascribed to some of the phenol oxidation to benzoquinone, followed by the reduction to hydroquinone, respectively.

With the addition of phenol to a solution containing acetonitrile and aqueous acid, there was a notable peak shift towards a lower oxygen overpotential in the forward scan direction. The reverse scan showed a slightly broader oxidation peak with no distinctive peak to indicate the oxidation of the phenol. One can assume that the oxidation of the phenol would be occurring within the broad observed peak. The reduction of the benzoquinone to the hydroquinone was also observed by a peak at a potential of 0.55 V. This shows that the aqueous solution containing a relatively high concentration of acetonitrile should be a suitable solution for the oxidation reaction of phenol on the electrode surface of  $\text{PbO}_2$ .

The initial results of the study showed relatively low conversion of the phenol with time as the solution flowed through the micro-flow cell, while the flow rates, acid concentration and cell potentials were adjusted to allow for the complete conversion of the phenol that was in the starting solution. In these studies, only the phenol concentration that remained in the final product stream solution relative to the 50 mM reactant stream was quantified. As an example, the results of observing the amount of phenol that remained at regular time intervals in the product stream with variation of the acetonitrile/water solution mixture and keeping all other conditions the same are shown in Fig. 8.

The results showed that the solution that contained the lower

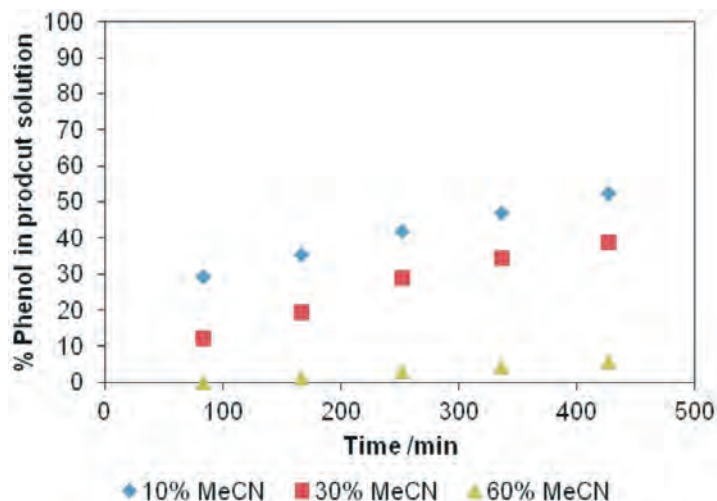


**Figure 7** Cyclic voltammogram of a  $\text{PbO}_2$  electrode in a water solution with 2% sulphuric acid with and without phenol. Also, a cyclic voltammogram in 60 acetonitrile/40 water solution with 2% sulphuric acid with 50 mM phenol only. All scans were relative to  $\text{Hg}/\text{Hg}_2\text{SO}_4$  (Sat  $\text{K}_2\text{SO}_4$ ) reference electrode.

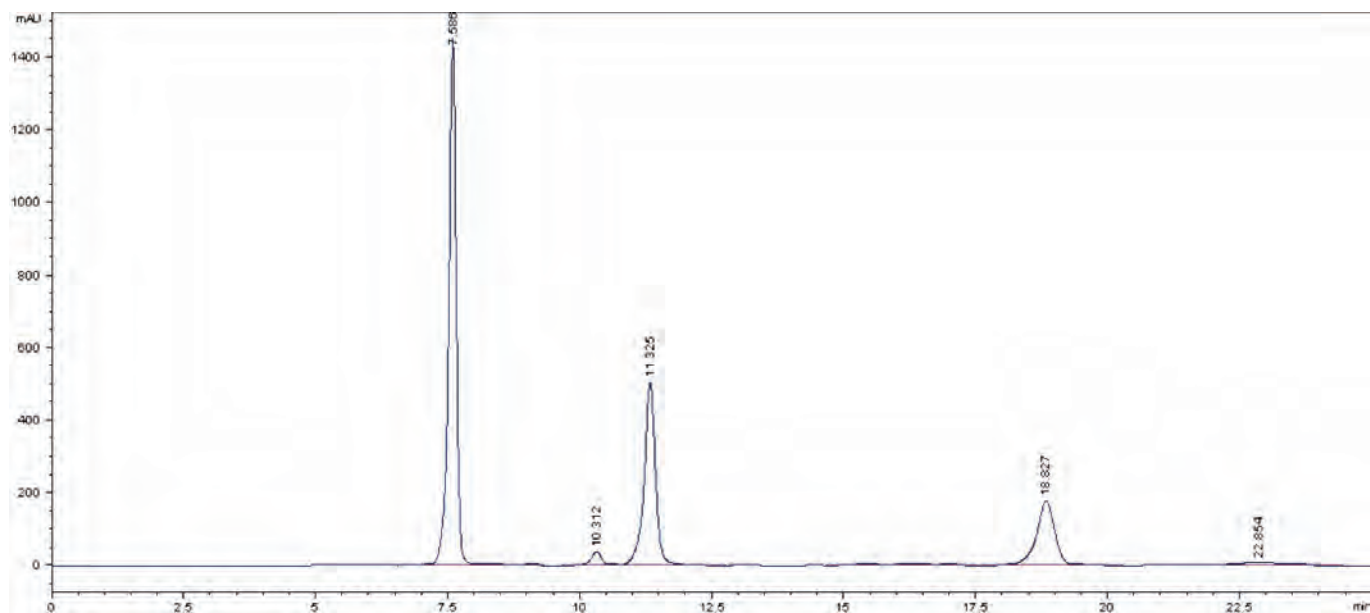
concentrations of acetonitrile would show a lower conversion of the phenol within the first few minutes of the solution mixture flowing through the reactor. The amount of phenol that remained in the product stream would subsequently increase, but after 400 min, more than 40% of the phenol remained in the product stream which contained only 10% acetonitrile. The results do not show the accumulated phenol that was in the final product stream but rather the phenol that was determined at the particular time interval being a representation of the solution flowing through the reactor. The results also showed that the solution containing 60% acetonitrile would be suitable for allowing almost all the phenol in the product stream to convert

over the time. After each experiment, the reactor was reconditioned, by allowing a 2% sulphuric acid aqueous solution to flow through the cell for about 3 h at a relatively high cell potential. This would allow any of the  $\text{PbSO}_4$  that had formed on either of the electrodes during the reaction process to convert back to the desired active material and to remove any unwanted polyphenols that might have formed on the electrode surface and end up clogging the porous structure.

Once the various parameters were optimized, the long-term reactor stability of converting the phenol to the desired products was examined quantitatively by allowing the reactor to run continuously at the  $0.5 \text{ mL min}^{-1}$  flow rate for 400 min. Samples



**Figure 8** Phenol in final product solution mixture analyzed at regular time intervals



**Figure 9** Typical HPLC chromatogram showing the compounds in the product stream. The elution peaks were identified as: hydroquinone at 7.58 min, benzoquinone at 10.31 min, catechol at 11.33 min, phenol at 18.83 min and 4,4 biphenol at 22.85 min.

of the product stream were taken at regular intervals and their content and respective concentrations were determined by HPLC analysis. The HPLC chromatogram of a typical product stream sample is shown in Fig. 9, indicating that the main components separated completely with no peak overlaps.

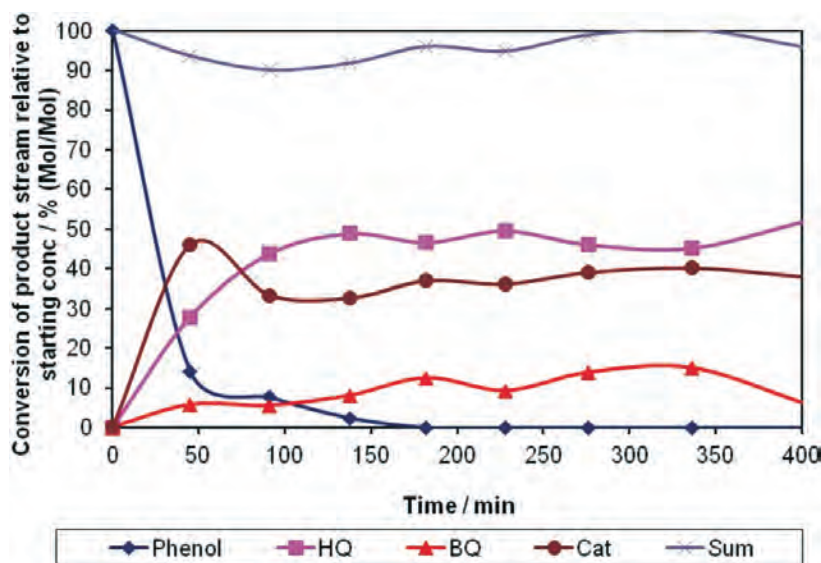
The observed reaction products were quantitatively analyzed for their mole content relative to the initial phenol that was in the reactant solution (Fig. 10).

The sample at time zero was that of the initial sample before it had gone through the micro-flow reactor. Sample aliquots (5 mL) were taken at regular time intervals, this being a representation of the product stream composition after the continuous flow through the reactor. It was not a representation of the accumulative product collected after the specific flow time. The sum of the products would average to about 95 % showing that there was a reasonably good mass balance between the reactant (phenol) and products. Other possible products that were not quantified could be biphenols, organic acids and CO<sub>2</sub>. Over the

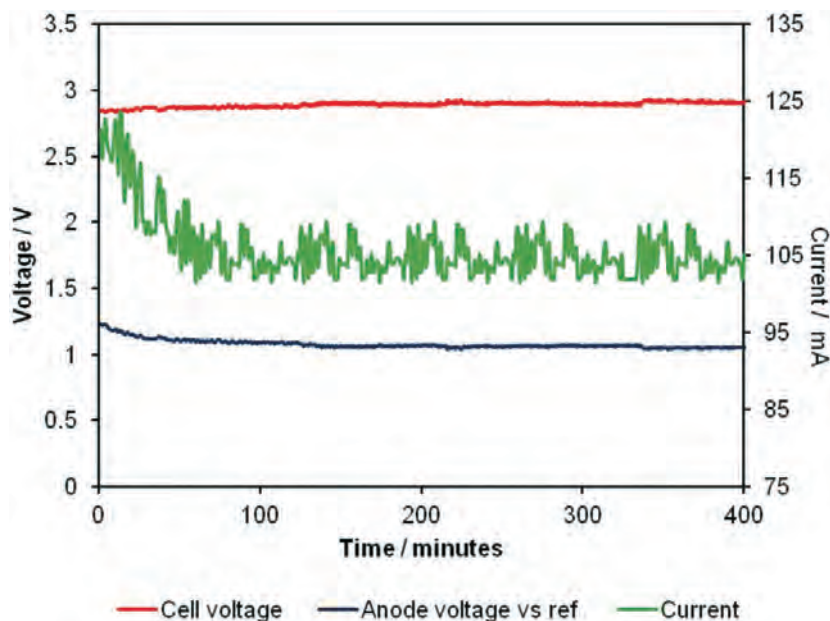
400 min of reaction time through the reactor, the cell current, cell voltage and anode voltage *vs.* the reference electrode were recorded (Fig. 11). Qualitative sampling was done at the 'sampling outlet' of the product stream before the cathode (Fig. 4). The results showed that the solution contained predominantly benzoquinone before it entered the sponge Pb electrode.

The results showed that as the phenol was introduced into the reactor cell; a slightly higher current of about 122 mA was observed within the first 50 min, which over time decreased to an average of about 106 mA. The current stabilized and remained relatively constant for the duration of the experiment showing that a dynamic equilibrium of the system was achieved between the conversion of phenol and that of the energy input. In terms of the coulombic energy used over the 400 min, a total of 2540 C was required.

With an average of 97 % phenol conversion over the 400 min, a total of 9.8 mmol (97 % of 10.1 mmol) of phenol would be equivalent to 1822 C theoretical requirements. Since this was lower



**Figure 10** Change in the amounts (% mol/mol) of the main reaction products relative to the initial phenol concentration in the initial reactant solution.

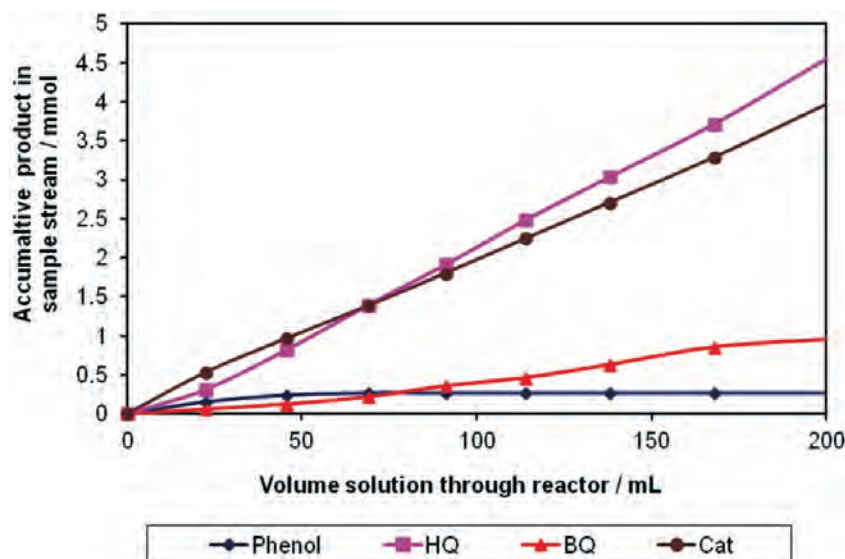


**Figure 11** Comparison of the current consumed and the respective cell and anode voltages over a continuous flow reaction time of 400 min. The anode potential measured *vs.* Hg/Hg<sub>2</sub>SO<sub>4</sub> (Sat K<sub>2</sub>SO<sub>4</sub>) reference electrode.

than the observed coulombs consumed, a certain amount of current was used for other side-reactions not considered in the phenol oxidation and benzoquinone reduction. These could include water electrolysis, formation of larger biphenols and other reactions products such as CO<sub>2</sub>. The quantitative analysis of the product stream can also be expressed as the accumulative main products in the final product volume solution over the reaction time of 400 min (Fig. 12).

The results from the accumulated product solution showed that some phenol was observed during the initial stages of the solution flowing through the reactor. Notably there was some benzoquinone observed in the product stream which seemed to increase towards the end of the 400 min (200 mL total product stream). This implied that some of the material was passing through the cathode without being reduced. This can be alleviated by increasing the cathode plate size, which in this case was only 4 mm thick. Also, the sponge Pb electrodes used in the Pb-acid battery industry are generally not as densely packed as the constructed anode used in this study. The results also

showed that during the initial stages of the reaction process, the catechol in the product stream was slightly higher than the corresponding hydroquinone, which over the 400 min seemed to decrease with a corresponding increase in the hydroquinone product. The total moles of phenol that flowed through the cell was equivalent to 10.07 mmol. The accumulative mmol of product that formed would add up to 9.77 mmol leaving a difference of about 0.30 mmol. The unaccounted quantity was most probably due to other side products not considered in the quantification that would include biphenol, the formation of maleic acid and CO<sub>2</sub> (Fig. 1), which was observed in some of the HPLC analyzes (Fig. 9). The quantification of the biphenol was not done in this study due to the relatively small HPLC peak that was only occasionally observed during the sampling stages. In the HPLC chromatogram, there were also other smaller peaks observed near the hydroquinone and catechol main product peaks that were not qualified in this study. These could be other by-products that were reported by others in the oxidation of phenol.<sup>8</sup>



**Figure 12** Accumulative reaction product in the final solution that passed through the micro-flow reactor.



#### 4. Conclusion

This study showed the working principle of a micro-flow-through electrochemical cell for converting phenol to hydroquinone and catechol. The construction of the electrodes of the cell was made by using the traditional processes for the active material used in the manufacturing of electrodes for Pb-acid batteries. This resulted in a relatively low-cost three-dimensional micro-porous electrode with a high SA:V ratio. The current collectors and electrode active material are made from Pb and PbO powder that can be easily worked into any desired cell size or configuration. The compressing and packing of the oxide powder can be easily adjusted to result in a more or less dense packed electrode that would rely on traditional curing and formation processes used in the Pb-acid battery industry.

By adjusting the applied cell potential, flow rates and solution composition, which in this case was an acetonitrile/water mixture, the conversion of phenol to its desired products can be controlled and optimized. The main products observed in this study showed the working principle of a continuous flow process that can convert reactants such as phenol to desired hydroquinone and catechol products. The process can be easily improved and scaled up by changing the packing density of the active material and possibly using large-scale industrial type battery electrodes commonly made by the local Pb-acid battery manufacturer. The effectiveness of the continuous process can be further demonstrated by removing the desired final products of the hydroquinone and catechol by precipitation from the product solution stream, where the solvent can then be reused.

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