



Evaluation of PEMFC System Contaminants on the Performance of Pt Catalyst via Cyclic Voltammetry

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Evaluation of PEMFC System Contaminants on the Performance of Pt Catalyst via Cyclic Voltammetry

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Abstract. Using cyclic voltammetry as a quick ex-situ electrochemical screening tool, the impact of the extracted solution and the individual leachable constituents from prospective balance of plant (BOP) component materials on the performance and recoverability of the platinum catalyst were evaluated. Taking an extract from Zytel™ HTN51G35HSLR (PPA) as an example, the major leachable organic components are caprolactam and 1,6 hexanediol. While these organic compounds by themselves do poison the Pt catalyst to some extent, such influence is mostly recoverable by means of potential holding and potential cycling. The extracted solution, however, shows a more drastic poisoning effect and it was not recoverable. Therefore the non-recoverable poisoning effect observed for the extracted solution is not from the two organic species studied. This demonstrates the complexity of such a contaminant study. Inorganic compounds that are known poisons like sulfur even in very low concentrations, may have a more dominant effect on the Pt catalyst and the recoverability.

1. Introduction

Low cost balance of plant (BOP) materials must be used in order to decrease the cost of fuel cell systems. Low-cost materials are typically required in consumer automotive markets, but lower cost typically implies higher contamination potential. Selection of such low-cost materials for system components requires an understanding of the materials and the potential contaminants that evolve from them. System contaminants have been shown to affect the performance and durability of fuel cells (1,2). Using cyclic voltammetry as a quick and cost-effective ex-situ electrochemical screening tool (1-9), the present work evaluates the impact of the extracted solution and the individual leachable constituents from prospective BOP component materials on the electrochemical performance and recoverability of the platinum catalyst.

The Zytel™ HTN51G35HSLR, a polyphthalamide (PPA) material was used as a case study. According to the manufacturer (DuPont), this structural material is stable in fuel cell operating conditions and relative inexpensive compared to other automotive grade thermoplastics, which makes it attractive for fuel cell applications.

2. Experimental

The BOP material was aged in DI water at 90°C for six weeks, and typically 600 cm² of surface area of the material is soaked in 400 ml DI water (1). The total organic carbon (TOC) of the extracted solution is analyzed by means of Sievers InnovOx Laboratory TOC Analyzer (GE). The organic model compounds were identified using gas chromatography-mass spectrometry (GC-MS) (Agilent MSD5975C, GC7890A). (3,6,7).

The electrochemical experiments were carried out with a portable WaveNow potentiostat (Pine Instruments), controlled by a computer, at room temperature. The investigation utilizes conventional 3-electrode system, including a polycrystalline Pt rotating disk electrode (RDE) with a diameter of 5.0 mm as the working electrode (WE), a Pt mesh as the counter electrode (CE) and a Ag/AgCl electrode (SSE) as a reference (RE). The RDE typically has a surface roughness factor of 1.3 to 1.7. The SSE electrode was calibrated frequently with a reversible hydrogen electrode (RHE) in the same electrolyte, thus all potentials are referenced to RHE.

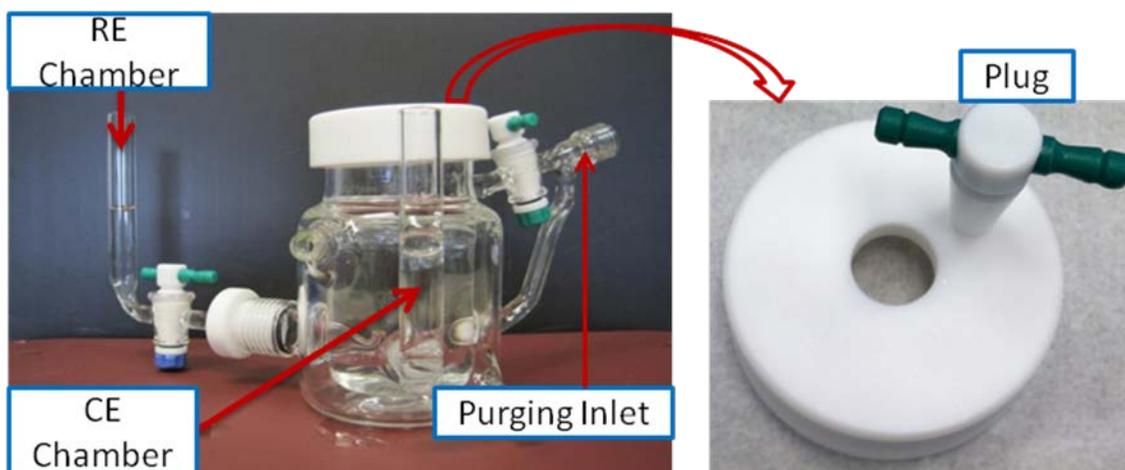


Figure 1. Cell (left) and cap (right) used for the electrochemical test.

Figure 1 shows the special cell design (volume 120 ml) for the electrochemical test. To prevent possible cross-contamination, it has a separate CE chamber and a separate RE chamber connecting the cell via a salt bridge. Purging gas can be introduced either through the bottom part or from the top part of the cell. Before the electrochemical measurements, the cell was cleaned in concentrated acids with the previous procedure (4). The electrolyte solution was 0.1M HClO₄, prepared using 18 MΩ deionized (DI) water. The solution was purged thoroughly with research purity nitrogen gas (99.9999%) for at least 30 min before the test. During the experiment, the same gas was purged above the electrolyte solution. The inert gas blanket was used to block the air into the cell.

Pt RDE was first conditioned by scanning between 0 to 1.1 V at 500 mV/s for at least 500 cycles, until reproducible cyclic voltammetry (CV) curves of a clean polycrystalline Pt were obtained. Partial baseline CV was performed immediately in the potential range of 0.05V to 0.55 V at a rate of 100 mV/s. A full baseline CV was done immediately in the range of 0.05V to 1.05V at the same rate. The electrochemical surface area (ECA) is calculated by integrating the CV in the hydrogen adsorption region. Then, a pre-determined amount of extracted solution(s) or a model compound was injected into the

electrochemical cell through the hole in the cap (Figure 1 right). In this step, the Pt RDE was held at 0.4 V for 30 seconds and rotated at 2500 rpm while the solution was purged with nitrogen gas from the cell bottom. A control test with DI water under identical conditions showed that less than 5% error may be introduced by this procedure. Partial CV scans were carried out with the contaminants added and ECAs were calculated to compare with the baseline. The difference in ECAs with and without the contaminant is the calculated platinum surface coverage. The Pt RDE was then carefully moved from the contaminated solution, rinsed with DI water and put into another cell (cell 2) with clean electrolyte. The second cell was purged with nitrogen for at least another 30 minutes. Partial CV scans were carried out to determine the ECA. Potential holdings at 0.75 V, 0.85 V, 0.95 V and 1.05 V, for 5 minutes each, and potential cycling between 0.05 and 1.05 V for 10 cycles at 100 mV/s were performed to investigate the recoverability of the Pt surface area loss.

3. Results and Discussions

3.1 BOP Leaching Extracts and Effect on CV

The aqueous extract from the Zytel™ HTN51G35HSLR material was analyzed using several analytical techniques. The measured total organic carbon (TOC) of the aqueous extract solution was 94.3ppm. The solution conductivity of the extract was 240.4 $\mu\text{S}/\text{cm}$. The major leachable organic components from the Zytel™ HTN51G35HSLR material were ϵ -caprolactam ($\text{C}_6\text{H}_{11}\text{NO}$) and 1,6-hexanediol ($\text{C}_6\text{H}_{14}\text{O}_2$), with an approximate ratio of 3 to 2 based on the peak areas as determined by GC-MS analysis. Figure 2 shows the chemical structures of these two model organic compounds.

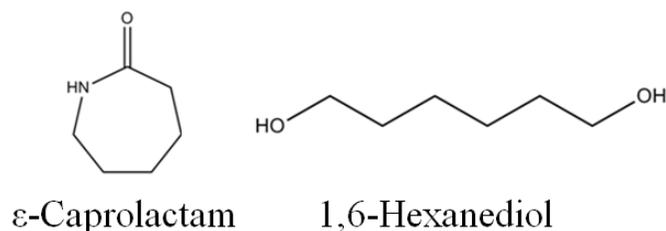


Figure 1. Chemical structure of ϵ -caprolactam and 1,6-hexanediol.

Reproducible partial baseline CVs for a clean polycrystalline Pt in a fresh 0.1 M HClO_4 acid solution are shown as dotted purple curves in Figure 3a. After 3.85 ml of extract solution Zytel™ HTN51G35HSLR was added to the electrolyte, the area under the partial CVs shrunk and the hydrogen adsorption peaks disappeared (solid black curves in Figure 3a). This volume was determined for a 50000:1 carbon to Pt site ratio, based on TOC, for reaching a steady state surface coverage quickly. The added Zytel™ HTN51G35HSLR extracts resulted in a decrease in the Pt ECA. Based on ECA in the full baseline CV, the surface coverage due to the extract is calculated and plotted in Figure 3b. The control test with DI water showed minimal ECA loss (<5%) within the same experimental time frame. About 85% of Pt surface was covered by the extract and this coverage reached steady state very quickly.

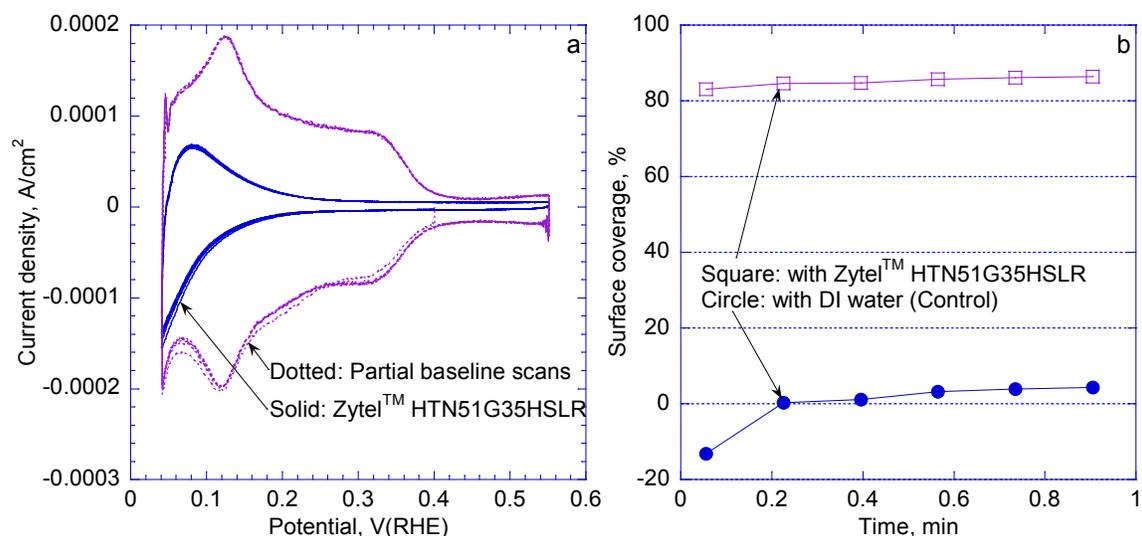


Figure 3. (a) Partial baseline CV at 100 mV/s (dotted) compared to the partial CV after exposure to 3.85 ml Zytel™ HTN51G35HSLR extract (solid); (b) The effect of Zytel™ HTN51G35HSLR extract on the Pt surface coverage (open squares). Control test results with DI water in blue solid circles are shown for comparison.

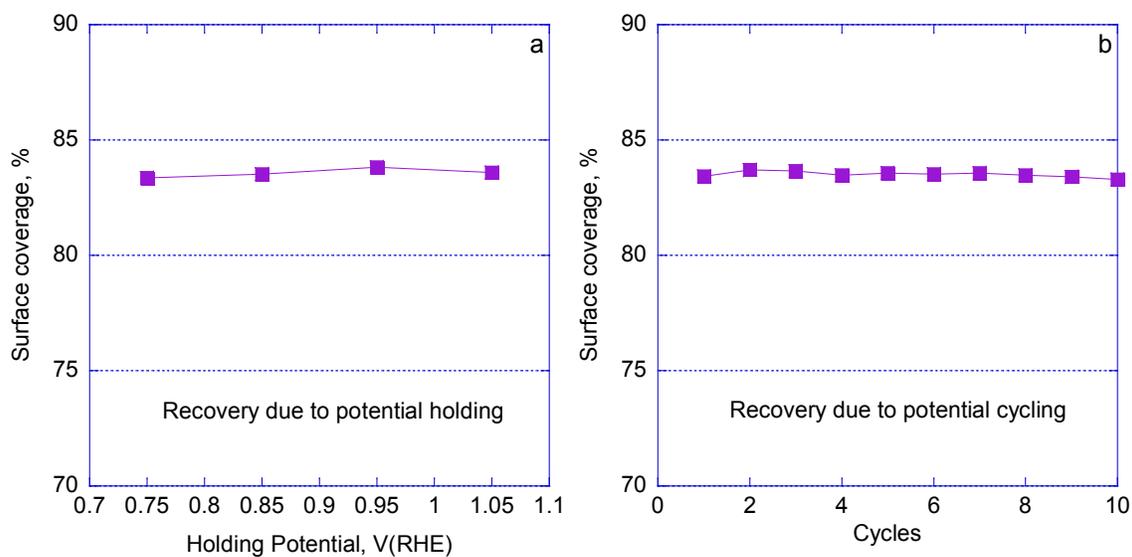


Figure 4. Recovery of Pt surface area was not achieved from potential holding (a) or potential cycling (b).

The contaminated Pt RDE was moved to a clean cell with fresh 0.1M HClO₄ solution and experiments were carried out to determine the recoverability of the Pt electrode. Figure 4a shows that the surface coverage of the Pt RDE was relatively unchanged by potential holding (5 minutes at 0.75V through 1.05V) and potential cycling (10 cycles between 0.05 to 1.05V) (Figure 4b). The Zytel™ HTN51G35HSLR extracted solution had a drastic poisoning effect on the Pt electrode and this poisoning effect was not recoverable. The final recovery scans were compared with the full baseline CV obtained at the beginning of the experiment in Figure 5. It can be seen that the contaminants in the

Zytel™ HTN51G35HSLR extracts impeded both the formation and reduction of Pt oxide and the hydrogen adsorption and desorption processes.

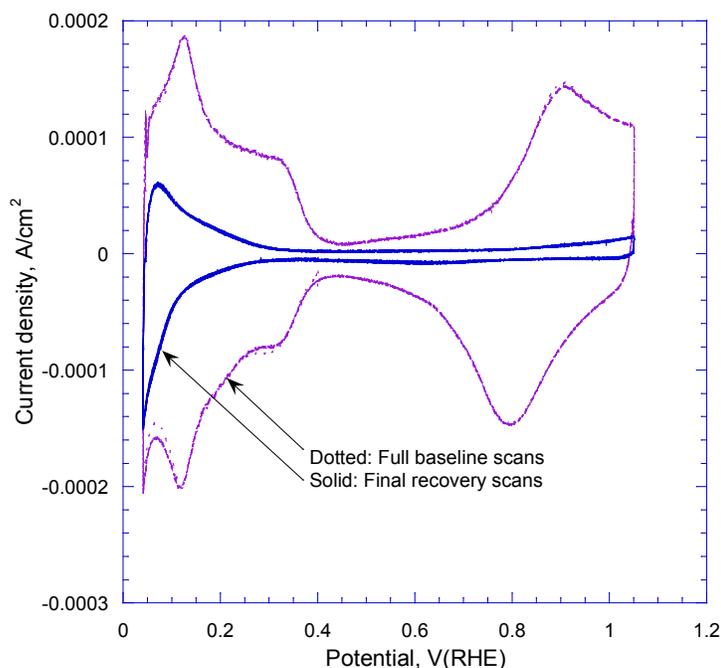


Figure 5. Full baseline CV scan (dotted) and the final recovery CV scans (solid) after the polycrystalline Pt RDE was exposed to Zytel™ HTN51G35HSLR extract and experience various high potential holding and cycling.

3.2 CV Characterization of the Model Compounds

CV characterizations were carried out with individual model compounds and with the two of them mixed together to gain a better understanding of the poisoning effect of the individual organic species and their interactions. When an individual model compound with corresponding amount to that in the Zytel™ HTN51G35HSLR extract was added, a loss in Pt ECA resulted. Figure 6 shows the percentage of the Pt surface covered by hexanediol (32-39%) and caprolactam (9-15%), compared to the DI water control. The higher surface coverage observed for hexanediol may be due to the fact that it is a short chain molecule, with less steric hindrance than a caprolactam ring molecule, and thus can occupy more Pt sites. The poisoning effect observed by these individual organic species are much less than that obtained for the extract solution.

The poisoning effect of both hexanediol and caprolactam were recoverable, based on the potential holding and potential cycling experiments carried out. The recovery results for hexanediol are shown in Figure 7. Figure 8 shows the final recovery scans of a hexanediol-contaminated Pt RDE compared to the full baseline CV for a clean Pt RDE. Figure 8 clearly shows that the Pt sites have been recovered, in contrast to the recovery CVs obtained for the extracts (Figure 5). Similar results were obtained for caprolactam (not shown).

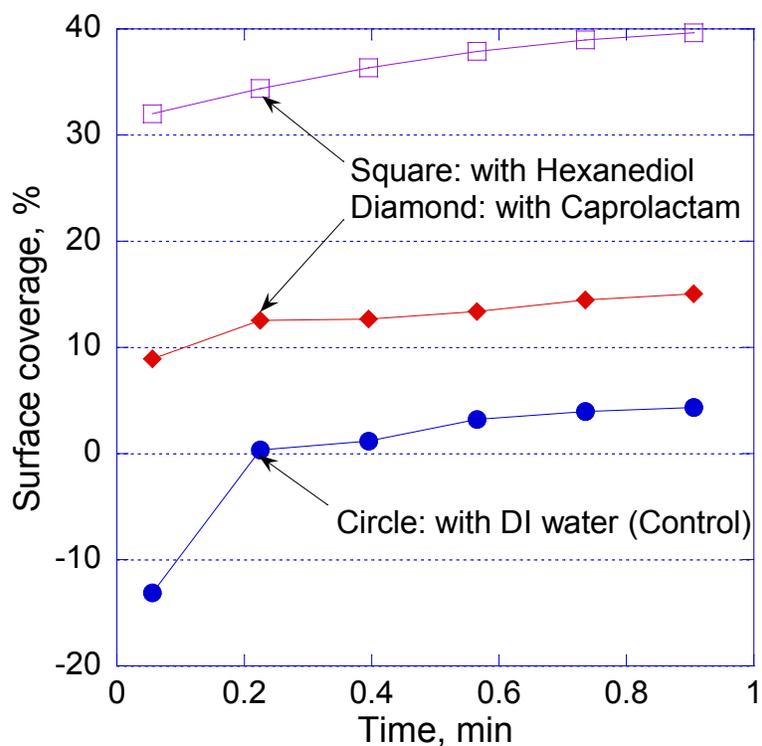


Figure 6. The poisoning effects of caprolactam and hexanediol, carried out in separate experiments, on the Pt sites.

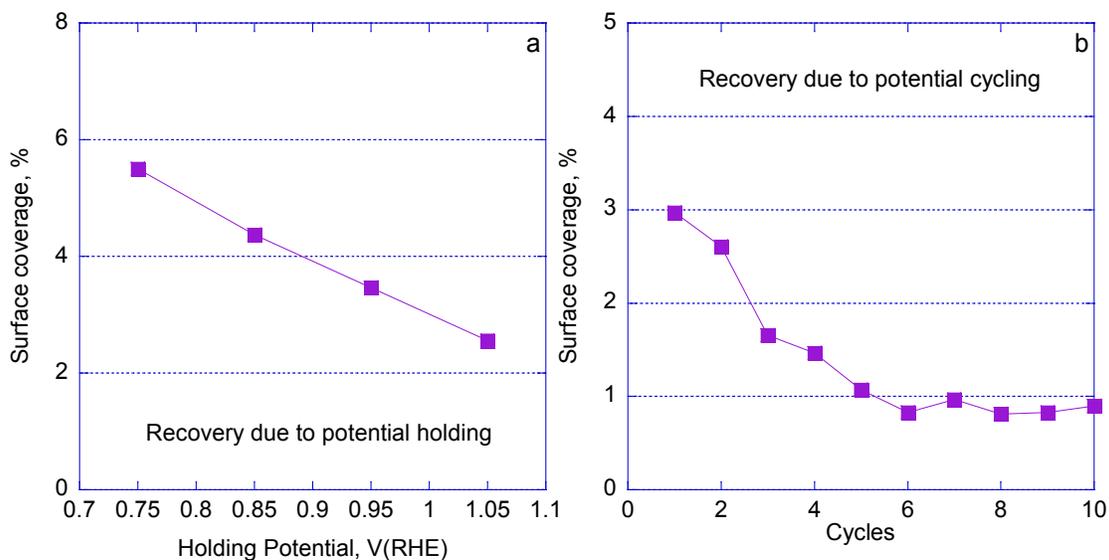


Figure 7. Recovery of the Pt sites resulting from potential holding (a) and potential cycling (b) for hexanediol.

When a mixture of hexanediol and caprolactam were added to the electrolyte, it is interesting that the poisoning effect observed (Figure 9) for the mixture was similar to that observed for the hexanediol alone (Figure 6). In both cases, 30-40% of the Pt surface was covered by the organic species and the essentially all Pt sites were recovered with

potential holdings and potential cycling, as indicated by the final recovery scans shown in Figure 10.

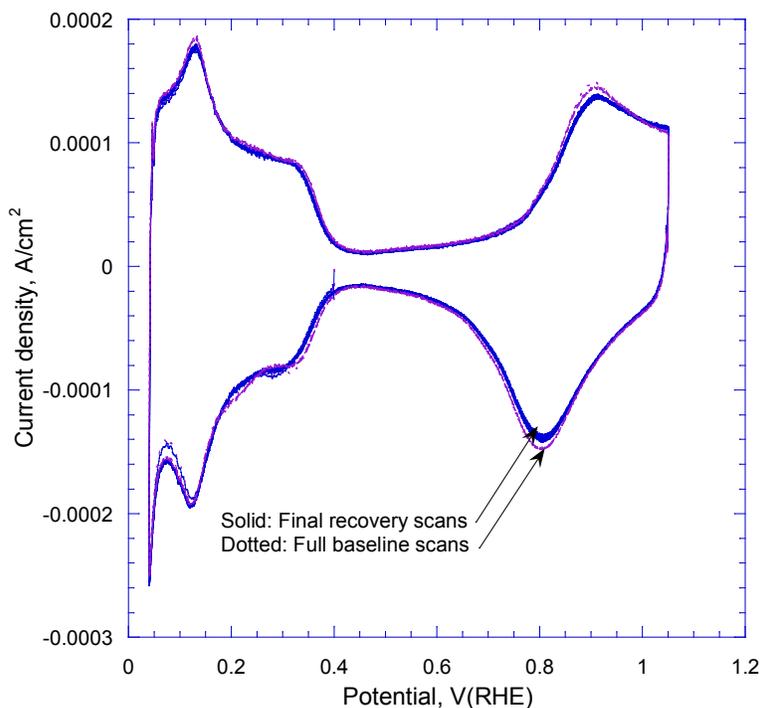


Figure 8. Full baseline CV scan (dotted) compared to the final recovery CV scans after Pt RDE was exposed to the hexanediol model compound (solid).

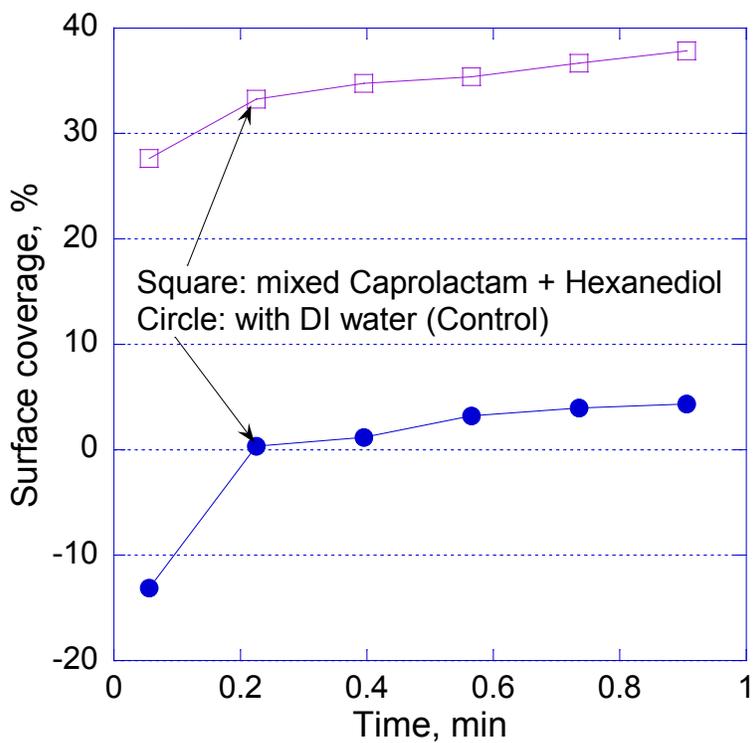


Figure 9. Pt surface coverage due to exposure to a mixture of caprolactam and hexanediol (open squares).

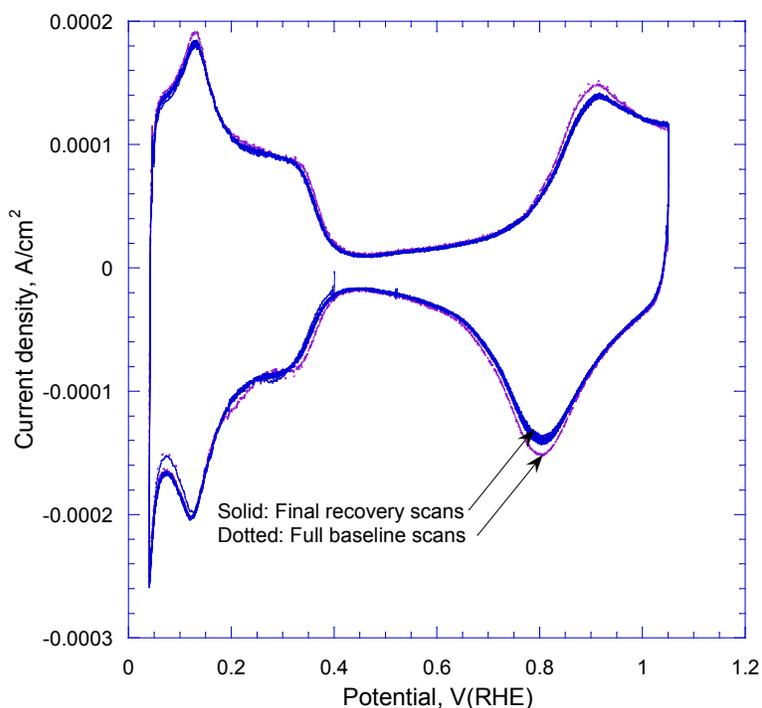


Figure 10. Full baseline CV scan (dotted) compared to the final recovery CV scans (solid) after the polycrystalline Pt RDE was exposed to a mixture of caprolactam and hexanediol.

3.3 Effect of Inorganics

From the results presented above, it can be concluded that the poisoning effect observed for the Zytel™ HTN51G35HSLR extracted solution is not from the two organic species studied. Unlike the unrecoverable poisoning effect of the extract solution, the organic contaminants, both individual and as mixtures, poisoned the Pt RDE to a lesser extent and the effect is recoverable. This demonstrates the complexity of a BOP extract contaminant study.

Inductively coupled plasma (ICP) was used to identify the elements present in the BOP extract solution, in addition to the organic species identified by GCMS. ICP analysis of the extract identified Ca, K, Na, and Si as major elements, with K having the highest concentration (37.34 ppm). The same CV procedure was used to investigate effect of K, using the same concentration measured by ICP. Potassium hydroxide was used as the K⁺ source. The CV results showed that the effect of K⁺ on Pt CV was minimal and that it was recoverable (not shown).

Careful inspection of the ICP results showed a small amount of S (0.227 ppm) present in the Zytel™ HTN51G35HSLR extract. Based on this sulfur concentration, an equivalent amount of 2.73×10^{-8} moles of sulfur is present in 3.85 ml of the Zytel™ HTN51G35HSLR extract solution. The available Pt sites on the RDE surface is ca. 6.0×10^{-10} molar (calculated from full baseline CV). Assuming one S binds to one Pt site, the sulfur amount in the extract solution is approximately 45 times more than the available Pt sites. This is certainly enough S to adversely affect the Pt electrode, since sulfur is a known contaminant that poisons Pt catalysts (10-12). ICP analysis, however,

does not tell us the oxidation state of S nor the type of S species in the extract solution. Due to lab safety restrictions, we were not able to study sulfur species like H_2S and SO_2 . Hence, we selected H_2SO_3 as the S species we will investigate using the same CV protocol.

To compare the effect of S species to that of the extract on the Pt electrode, an equivalent amount of sulfur (in the form of H_2SO_3) was added to the electrolyte and the poisoning effect of H_2SO_3 is shown in Figure 11. Within less than one minute, up to 75% of the Pt RDE was covered and surface coverage continued to increase with time. In fresh electrolyte, the contaminated Pt RDE could not be recovered by means of potential holdings and potential cycling. The final recovery scans (Figure 12) showed that the poisoning effect of H_2SO_3 is permanent and that the CV features are similar to the final recovery scans for the Zytel™ extracts. This suggests that the irrecoverable poisoning observed for the extract may be related to sulfur species. The fact that there are some subtle differences in the hydrogen adsorption region suggests a different form of sulfur is in the extract.

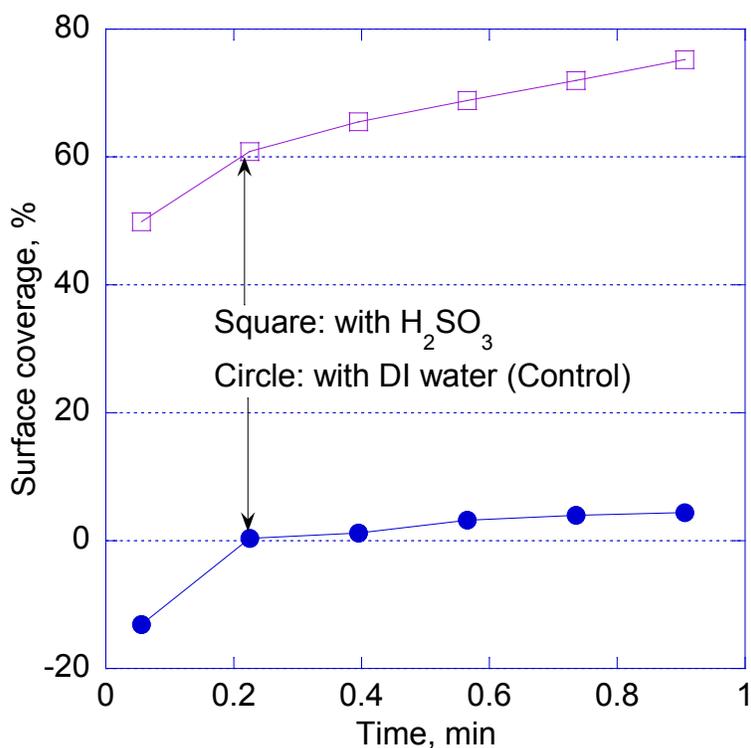


Figure 11. Pt surface coverage due to exposure to H_2SO_3 (open squares) compared to DI water control experiment (solid circle).

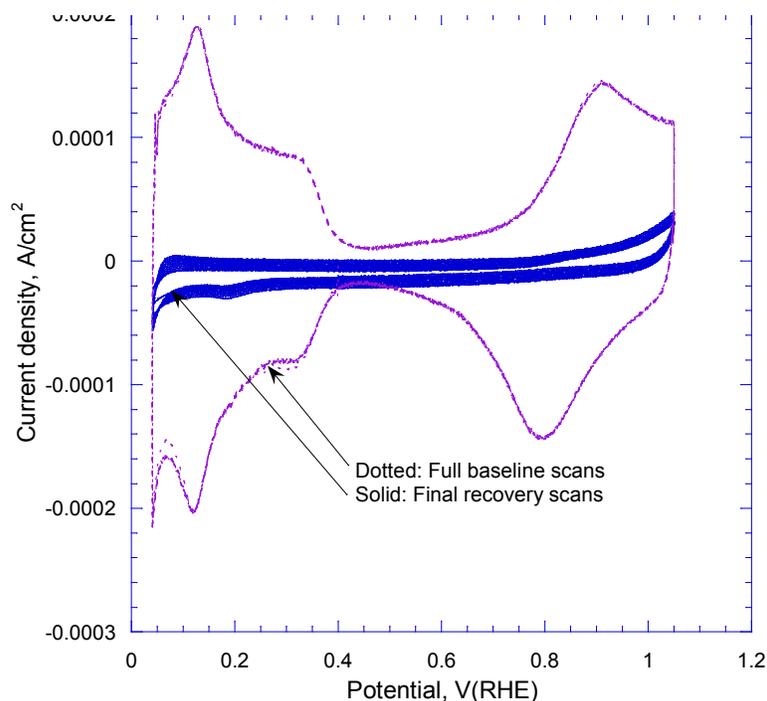


Figure 12. Full baseline Pt CV (dotted) compared to the final recovery CVs (solid) after Pt RDE was exposed to H_2SO_3 .

4. Conclusions

The impact of the extracted solution and the individual leachable constituents from a prospective BOP component material, Zytel™ HTN51G35HSLR, on the performance and recoverability of the platinum catalyst was evaluated. The major leachable organic components were caprolactam and 1,6 hexanediol. The electrochemical screening results showed that these organic compounds, studied individually and as a mixture, do poison the Pt catalyst to some extent but the effect is mostly recoverable by means of potential holdings and potential cycling. On the other hand, the extracted solution showed a more drastic poisoning effect and it was not recoverable. It was concluded that the irrecoverable poisoning effect observed for the extracted solution was not due to the two organic species studied. The effect of two inorganic species, K and S, was also studied since ICP results indicated the presence of these elements. The K^+ showed minimal effect while H_2SO_3 showed irrecoverable poisoning similar to the extracts. This study demonstrated the complexity of a system contaminants study. The effect of both the organic and inorganic species in the system contaminants must be considered, even if a very small amount is present.

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