## Modeling Analysis of Electrode Fouling due to Electro-Oxidation of Phenols

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Phenolic compounds, such as phenol and cresol, represent a chemical class widely utilized in industry and are chemical pollutants of the atmosphere, water systems, and many food products [1]. Tricresyl phosphate (TCP), a potential contaminate in an aircraft cabin [2, 3], is one of the harmful derivatives of these compounds. Therefore, electrochemical detection and disposal of phenols are very important and has long been of interest. However, electrode fouling (electrode passivation) due to the electro-oxidation of phenols is one prime problem during these processes. Electrode fouling is characterized by the occurrence of current decay during repetitive potential scans, continuous flow, or injections of samples. It is often caused by the formation of a passivating polymeric on film the electrode surface due to the electropolymerization of phenolic radicals. Although in some cases, this polymeric film can act as a protective coating and prevent metals from corroding, the electrode fouling is often a serious problem.

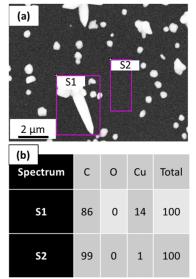
The mechanism of how the polymeric layer causes electrode fouling is of great interest. Several models have been reported with the aim of explaining the fouling effect, such as the "area blocking"/"active site poisoning" model [4], "film diffusion" model [5], and a semiempirical model based on electron tunneling and the Tafel equation [4]. However, none of them are capable of explaining the amperometric current decay for continuous flow of phenols at a constant oxidation potential. The present work utilizes a Cu deposition method, which is one type of metal decoration that has been used for pinhole mapping and the analysis of electrode surfaces, to study the mechanism of electrode fouling (Fig.1). Cresol was used as a representative phenolic compound.

It was found that the potential drop across the fouling layer was the main reason for current decay. Using the Cu deposition method and mathematic derivation of data, the potential drop was quantitatively determined. Finally, a model based on potential drop across the fouling layer has been developed, which was able to simulate and predict the fouling current in the term of applied potential and the flow time of cresol (Fig.2).

- Heras, M.A., et al., A poly(3,4ethylenedioxythiophene)-poly(styrene sulphonate) composite electrode coating in the electrooxidation of phenol. Electrochimica Acta, 2005. 50(7-8): p. 1685-1691.
- Yang, X., et al., Portable and remote electrochemical sensing system for detection of tricresyl-phosphate in gas phase. Sensors and Actuators B: Chemical, 2012. 161(1): p. 564-569.
- Simonian, A., G. Vertelov, and W. Gale, *Electrochemical Detection of Tricresyl Phosphate.* ECS Trans, 2006. 3: p. 21-34.
- 4. Gattrell, M. and D.W. Kirk, A Study of Electrode Passivation during Aqueous Phenol Electrolysis.

Journal of The Electrochemical Society, 1993. **140**(4): p. 903-911.

Babai, M. and S. Gottesfeld, *Ellipsometric study* of the polymeric surface films formed on platinum electrodes by the electrooxidation of phenolic compounds. Surface Science, 1980. **96**(1-3): p. 461-475.



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Figure 1. Observation of Cu deposition on glassy carbon electrodes with SEM (a) and EDS (b).

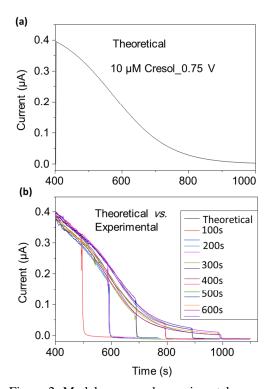


Figure 2. Model curve and experimental curves of cresol fouling. (a) One example of the theoretical current decay during amperometric analysis of cresol. (b) The comparison of theoretical and experimental current curves for analysis of 10  $\mu$ M cresol at 0.75 V. The theoretical curve overlapped others.