

Qualitative and Quantitative Information on the Role of Anions in Mechanisms for the Electrochemical Oxidation of Oxygenated Organics

Mark Schell and B. E. Kumara Swamy
The Department of Chemistry, Southern
Methodist University,
Dallas Texas 75275 USA

Several results are presented on how anions affect the electrochemical oxidation of oxygenated organic molecules. Some results are contrary to the current understanding of the effects of anions and anion adsorption on reaction pathways [1-5]. These results include ways anions affect reactions mechanisms that are different from geometric properties [6] and from blocking reaction sites [1], and demonstrating that increasing the solution's overall anion adsorption strength can increase the efficiency of reactions. Evidence is also presented that supports the idea that anions can produce an effect similar to that contained in the bifunctional theory [7-9] which describes how adatoms enhance reaction. The results are obtained through straightforward applications of simple electrochemical techniques and using techniques from nonlinear chemical dynamics [10-11].

The electrolyte has a direct effect on the efficiency of the electrochemical oxidation of oxygenated organics including fuel-cell reactants [1]. The anion adsorption strength is an important quantity in judging the viability of an electrolyte that includes a specific anion. It follows from the current understanding and theories that the properties of the electrolyte improve as the anion adsorption strength decreases; the lower the anion strength the better the electrolyte. Chlorate anions have one of the lowest adsorption strengths and that is why perchloric acid is usually the electrolyte of choice amount researchers.

Instabilities that result from varying the fraction of an anion are characterized. Varying another anion in another limit can produce similar instabilities. These and other experiments show that anion adsorption strength is not responsible for these changes. Instead, it is the interaction of anions with other anions and the chemical interaction with other surface species that play the dominant role.

Results from both current control and potential control experiments show that an electrolyte can be made to make a reaction more efficient by increasing its overall anion adsorption strength. Under other conditions, reactions are made less efficient by decreasing the overall anion adsorption strength. These results are contrary to the present understanding of the effects of anions. The results depend on the anions. Increasing the fraction of sulfuric acid in a perchloric acid sulfuric acid electrolyte can increase the efficiency of a reaction. However, increasing the fraction of phosphoric acid in a perchloric acid-phosphoric acid electrolyte mixture seems to only decrease efficiency. The results also depend on the organic being oxidized. Increasing the fraction of sulfuric acid in a perchloric acid-sulfuric acid electrolyte can increase the efficiency of the oxidation of formic acid but this increase does not appear to increase the efficiency of the oxidation of methanol. The efficiency of methanol oxidation is increased if the (hydrogen) sulfate anions are replaced by fluoroborate ion.

Acknowledgment

This research was supported by the National Science Foundation, Grant No. CHE-9731060.

References

1. J. Sobowski, K. Franaszczuk, and K. Dobrowolska, *J. Electroanal. Chem.*, 330 (1992) 529.
2. R. Parsons, and T. VanderNoot, *J. Electroanal. Chem.*, 257 (1989) 9.
3. N. Li and J. Lipowski, *J. Electroanal. Chem.* 491 (2000) 95.
4. N. Markovic, and P. N. Ross Jr., *J. Electroanal. Chem.*, 330 (1992) 499.
5. N. Markovic and P. N. Ross Jr., *J. Phys. Chem.*, 97 (1993) 9771.
6. K. Lust and E. Lust, *J. Electroanal. Chem.*, 552 (2003) 129.
7. M. Shibata, N. Furuya, M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, 263 (1989) 97.
8. M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, 60, (1975) 267.
9. M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, 202 (1986) 125.
10. M. Schell, F.N. Albahadily, J. Safar, *J. Electroanal. Chem.* 353 (1993) 303.
11. S. Chen, T. Noles, and M. Schell, *J. Phys. Chem. A*, 104 (2000) 6791.