

### Magnetic Field Effects on the Chlor-Alkali Process

Shelley D. Minteer, David Capretto, Sarah J. Pasek, and Shana Reidy

Department of Chemistry  
Saint Louis University  
3501 Laclede Ave.  
St. Louis, MO 63103

The magnetic modification of electrochemical processes has two benefits: it increases the rate of the reaction kinetics of the electrochemical reactions and decreases the reaction kinetics of unwanted side reactions. Magnetic fields have been shown to increase and decrease electrochemical flux (current density) due to magnetohydrodynamic effects [1] and gradient magnetic field enhanced mass transport [2-5]. The key to both of these effects is the presence of paramagnetic reactants, products, or electrolytes. In the chlor-alkali process, there are no paramagnetic reactants, products, or electrolytes. Therefore, a magnetic field will not affect the hydrodynamics or mass transport of chloride ions and protons to the electrode surface. However, magnetic fields can affect the electron transfer rates through spin polarization [6-9]. This can in turn alter the reactions' pathways and product distributions of electron transfer reactions.

In this system, another crucially important effect that alters the overall reaction kinetics of a system is present. This effect is referred to as magneto-adsorption and magneto-desorption. When a molecule adsorbs to a catalyst surface, there is a partial electron transfer that occurs as they share electron density. This partial electron transfer is dependent on the external magnetic field if the adsorption/desorption process causes a delocalization of the charge density from the spin density. This effect is very common and has been seen for a wide variety of adsorbates and catalysts [10-17]. The effect is due to the s-d exchange interaction that causes an overall magnetization change during the adsorption/desorption process [15]. Magneto-adsorption and magneto-desorption effects are crucially important, because they can be easily tailored to a given reaction system by modifying the existing catalyst with additives for promoting and inhibiting the magneto-adsorption and magneto-desorption effects [15]. In theory, any adsorption/desorption limited electron transfer mechanism can be improved and its secondary reaction rates decreased by tailoring the existing catalysts with additives that promote the s-d exchange interaction for the primary reaction and inhibit the interaction for the secondary reactions.

The chlor-alkali process is an example of an electrochemical cell that could benefit from magnetic modification. Theoretically, the cell produces chlorine, hydrogen, and sodium hydroxide (called chlor-alkali's), but cell efficiency is compromised because of poor kinetics and selectivity. Electrochemistry historically has had very poor selectivity because standard reduction potentials of reactants are often too similar. Unwanted secondary reactions can occur at both the anode and the cathode, and these side reactions increase energy consumption and decrease efficiency. If magnetic modification of the chlor-alkali cathode and anode can increase kinetics, selectivity, and efficiency, then these steps will be less necessary.

In this paper, magnetic field effects on the anodic and cathodic half-cells of the chlor-alkali process are studied. The results show that substantial magnetic field effects are present in the half-cells of the chlor-alkali process.

Studies show that both the anode and cathode reactions of the chlor-alkali process can be enhanced significantly by magnetic modification of electrode surfaces. Bulk electrolysis studies of the chlor-alkali anode show that the flux (current density) of magnetically modified electrodes is a factor of  $3.22 \pm 0.08$  larger than the flux of non-magnetically modified electrodes. If the current density of a system increases, the power consumption of a reaction decreases, thereby, making a more energy efficient reaction.

The chlor-alkali cathode studies show that a magnetically modified electrode passes 91.4% more charge at the same potential as a non-magnetically modified electrode. More importantly, magnetically modified electrodes produce 64.6 times the  $\text{OH}^-$  of the non-magnetically modified electrodes (as determined by titration of the brine solution after electrolysis). Therefore, magnetic modification of the cathode can increase efficiency by increasing the production of hydroxide ion and decreasing the production of unwanted by-products.

### References

1. Grant, K.M.; Hemmert, J.W.; White, H.S. *J. Am. Chem. Soc.* **2002**, 124, 462-467.
2. Ragsdale, S.R.; Grant, K.M.; White, H.S. *J. Am. Chem. Soc.* **1998**, 120, 13461-13468.
3. Leventis, N.; Gao, X.; *Anal. Chem.* **2001**, 73, 3981-3992.
4. Pullins, M.D.; Grant, K.M.; White, H.S. *J. Phys. B* **2001**, 105, 8989-8994.
5. Leventis, N.; Gao, X. *J. Am. Chem. Soc.* **2002**, 124, 1079-1088.
6. Turro, N.J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, 13, 369-377.
7. Ronco, S.; Ferraudi, G. *J. Chem. Soc., Dalton Transactions* **1990**, 3, 887-889.
8. Ronco, S.; Ferraudi, G. *Inorg. Chem.* **1990**, 29, 3961-3967.
9. Minteer, S.D. Ph.D. Thesis, University of Iowa, 2000.
10. Ozeki, S.; Miyamoto, J.; Ono, S.; Wakai, C.; Watanube, T. *J. Phys. Chem.* **1996**, 100, 4205-4212.
11. Ozeki, S.; Uchiyama, H. *J. Phys. Chem.* **1988**, 92, 6485-6486.
12. Uchiyama, H.; Kaneko, K.; Ozeki, S. *Langmuir* **1992**, 8, 624-629.
13. Uchiyama, H.; Kaneko, K.; Ozeki, S. *Chem. Phys. Lett.* **1990**, 166, 531.
14. Ozeki, S.; Miyamoto, J.; Watanube, T. *Langmuir* **1996**, 12, 2115-2117.
15. Mikhalenko, I.I.; Yagodovskii, V.D. *Russian Journal of Physical Chemistry* **2000**, 74, S411.
16. Lin, P.; Peng, J.; Hou, B.; Fu, Y. *J. Phys. Chem.* **1993**, 97, 1471-1473.
17. Makarshin, L.L.; Andreev, D.V.; Parmon, V.N. *Physica C* **1997**, 282-287, 1609-1610.