Chlorine Reduction on Pt and Ru; Effect of Oxide Coverage

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Introduction

The chlorine electrode has a potential for use in fuel cells due to its fast kinetics and relatively high standard potential (1.36V vs. SHE) [1]. A H_2/Cl_2 fuel cell has the possibility of very high power densities and energy efficiencies. Due to the corrosive environment of this fuel cell, ordinary Pt catalysts are not stable and a substitute must be found.

The chlorine electrode is of great importance to the electrochemical industry and chlorine evolution has been studied extensively for many years [2-4]. Chlorine reduction however, has not been given much focus. The aim of this work is to increase the knowledge of the chlorine reduction mechanism on platinum and ruthenium with different oxide coverages and apply this in the development of new electrocatalysts for a H_2/Cl_2 fuel cell system

Experimental

A rotating-disc electrode with an electrode area of $0.28cm^2$ was immersed in a 1M HCl electrolyte saturated with Cl_2. The electrode was first brought to a reversible state of activity by cycling the electrode between 1,7 and 0V vs. Ag/AgCl and then pretreated at different potentials, producing various amounts of oxide on the surface. The current/potential curve between 0.9 and 1.125V was then recorded. This procedure was repeated for rotation rates from 200 to 6000rpm.

Results and Discussion

Figure 1 shows a plot of I^{-1} vs. rotation rate$^{-1/2}$. The rate constant, k, can be found using the slope and the intercept of the plot.

Figure 2 shows the variation of the rate constant for chlorine reduction as a function of electrode potential and pretreatment. Higher oxide coverage results in a lower rate constant due either to a change in mechanism or a change in the state of the oxide film and subsequently a different electrocatalytic activity for the Cl_2 reduction reaction [4].

The diffusion coefficient of chlorine in 1M HCl at 25° C was determined to $4.56 \cdot 10^{-5}$ $cm^2 s^{-1}$.

The determination of reaction orders with respect to chlorine, chloride and pH and the search for mechanisms that accord with the results is in progress.

Figure 1: I^{-1} vs. $\omega^{-1/2}$ at a series of potentials between 1.125V and 0.9V with a step of 25mV. Pretreatment: 1.6V 10s.

Figure 2: Rate constant for chlorine reduction on Pt as a function of electrode potential and pretreatment.
●: 0.9V 10s, ○: 1.6V 10s, ▼: 1.7V 10s, ▽ 1.8V 60s

References

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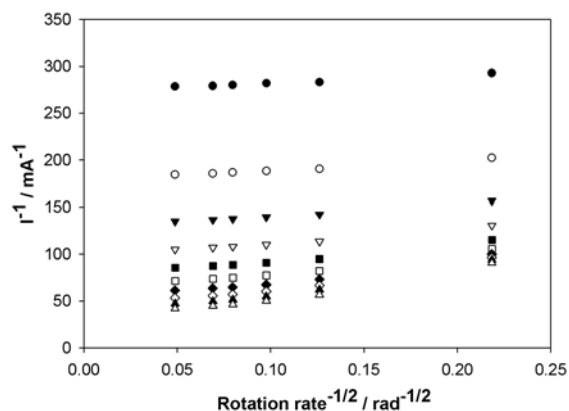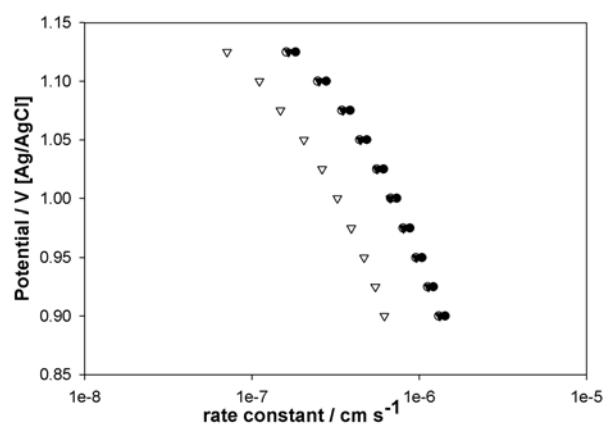[4] S.G. Roscoe, B.E. Conway, *J. Electroanal Chem.* 224 (1987)