

kinetic data should be obtained with a rotating cylinder electrode where the current distribution is more uniform.

- Kinetic rate data for the concentrated ferric-ferrous couple in concentrated acid chloride electrolytes is inconsistent with dilute solution area. The mechanism for charge transfer should be elucidated. Perhaps data at well-characterized noble metal electrodes will be necessary.
- Electrocatalytic surfaces are needed for the kinetically slower negative redox couples such as the chromic-chromous couple. These surfaces also must minimize the competitive proton reduction parasitic reaction. Previous electrocatalyst development work has almost completely neglected examining performance at elevated temperatures (greater than 60 °C) where the pentahydrate-monochloro complex of the chromic ion predominates. This form of chrome ion is known to be faster reacting, and electrocatalytic activity will be more pronounced because the reaction is thought to be through inner-sphere transfer. A systematic evaluation of the activity of carbon surfaces is needed. It should be worthwhile to pursue studies of surface treatments and modifications and then relate the electrocatalytic activity to the types of surface functional groups.

ELECTROCHEMICAL STORAGE CELL BASED ON POLYCRYSTALLINE SILICON

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This project is aimed at the selection of redox couples and solvents, development of corrosion inhibition for silicon, construction and evaluation of a test cell, and evaluation of a novel photoelectrochemical cell for solar energy conversion and storage.

SRI International conducted theoretical and experimental investigations on the performance of n- and p-type silicon in solution for efficient solar energy conversion.

In the experimental work an attempt was made to identify redox couples capable of inducing maximum band bending (highest open circuit voltage) and limiting the corrosion for both n- and p-type silicon. Measurements showed that high photovoltages could be obtained by using vanadium (II/III) and ferrocene/ferricenium couples for p-type and n-type silicon, respectively. With these systems, SRI demonstrated reasonable stability even though these couples were incapable of producing a high efficiency. The low efficiencies were caused by the growth of a relatively thick insulating SiO₂

corrosion layer. Under conditions of low light intensity, however, a thin (approximately 15 Å) SiO₂ layer enhanced the solar cell characteristics.

Corrosion studies were performed to evaluate the use of hydrofluoric acid to remove the corrosion layer. In these experiments, the interaction between HF and the redox couple was examined. High or low concentrations of HF accelerated the corrosion of the surface. Redox couples may play different roles in this corrosion: some redox couples are not affected by the HF and do not suppress corrosion, while others catalyze the corrosion of the semiconductor by HF.

Much of the experimental and theoretical work focused on the effect of the surface oxide on solar cell characteristics. These studies in turn led to a variety of surface treatments aimed at improving the fill factor of silicon photoelectrochemical cells. The surface treatments included high-temperature annealing of the normal oxide under an argon or hydrogen atmosphere, coating a p-n junction with a thin layer of platinum, and passivation with polyvinylcarbazole polymer.

The silicon electrode is subject to severe corrosion problems. This corrosion leads to highly insulating thin films of SiO₂, which block the photocurrent. Thus, the silicon electrode must be completely stabilized to realize high efficiency and acceptable cell life. Research indicates that the required stability will probably not be achieved on a bare Si surface.

Up to now, the most promising method for stabilizing the Si is by application of thin metal films. However, the use of conducting surface films leads to a loss of open circuit voltage because of enhanced dark currents. Thick layers of conducting material also block the incoming light. Further studies using less active conducting polymer films might lead to new stable systems, but at the present time, it appears that enhanced stability may be achieved only with a loss of efficiency.

Other semiconductor materials such as CdSe may be more promising. High photovoltages (approximately 1.0 V) and conversion efficiencies (approximately 12 percent single crystal) have been obtained. However, corrosion problems with this electrode have not been completely solved. It is clear that corrosion is the most important bottleneck to the development of devices utilizing the photoelectrochemical approach.

Recent publications

- 1 D. Canfield and S. R. Morrison, The effect of surface films on photoelectrochemical solar cell performance, *Appl. Surf. Sci.*, in press.
- 2 S. R. Morrison, Surface films on semiconductor, *American Chemical Society Meeting, Las Vegas, 1982.*