

TABLE 2

Diffusion coefficients of $\text{ZnCl}_2\text{-KCl-H}_2\text{O}$ at 25 °C (ZnCl_2 at 0.5 mol)

\bar{c}_1	\bar{c}_2	$10^5 D_{11}$	$10^5 D_{12}$	$10^5 D_{21}$	$10^5 D_{22}$	Comments
0.5	0.5	0.935	0.017	0.161	1.555	1982
0.5	2.0	0.954	0.041	0.047	1.542	1981
0.5	4.0	0.933	0.026	-0.700	2.003	preliminary

\bar{c}_1 and \bar{c}_2 are in mol-dm^{-3} ; D_{ij} are in $\text{cm}^2 \text{sec}^{-1}$; 1 refers to ZnCl_2 ; 2 to KCl .

values for all D_{ij} with 0.5 M ZnCl_2 are given in Table 2. In addition, 22 densities at various ternary compositions have been measured.

During 1983 more binary $\text{ZnCl}_2\text{-H}_2\text{O}$ D_{vs} will be measured with the purer ZnCl_2 to further check earlier measurements. Higher and lower concentrations will also be measured to characterize this salt more fully. One more ternary composition will be done to add to the grid of compositions needed to understand this exceptionally complicated system.

TRANSITION METAL OXIDE COATED TITANIUM ELECTRODES FOR REDOX BATTERIES

The University of Akron, Akron, OH 44325 (U.S.A.)

The objective of this research program is to ascertain electrocatalytic activity of transition metal oxides for use as long-life redox battery electrodes. A primary motivation for this work is to produce porous electrodes (of titanium) with reproducible surface activity for experiments to corroborate predictions of porous electrode theory. An additional goal of this research program is to ascertain whether a simple one-step outer-sphere electron transfer mechanism relates to the ferric-ferrous redox reaction at high reactant/product concentrations in a strong acid chloride medium. Kinetic rate expressions of this couple under these conditions at the metal oxide surfaces are sought.

Coatings of the conductive and active rutile structure form of selected transition metal oxides (namely RuO_2 , IrO_2 , OsO_2) are desired. Both IrO_2 and RuO_2 coatings having the rutile structure (as confirmed by X-ray diffraction) were prepared by thermal decomposition of their respective hydrated chloride salts. In the case of OsO_2 , only amorphous coatings have been achieved. Failure to obtain the rutile structure is apparently due to the conversion of OsO_2 to the volatile OsO_4 at baking temperatures. Further work with OsO_2 is not being pursued at this time.

The determination of the electrochemically active surface area is important in evaluating the intrinsic activity of electrode materials. Because variations in the coating techniques and in substrate condition along with handling and electrochemical history all markedly affect the true surface area, a measurement of the actual surface area of the rotating disk electrode (RDE) is required immediately prior to taking kinetic measurements. The voltammetric charge (0.05 to 1.0 V versus standard calomel electrode (SCE), 20 mV/s, in 1 M H₂SO₄ at 25 °C) is being used as a means of estimating the disk surface area. The correlation of charge with true surface area (as measured by Zn²⁺ adsorption) has been found using larger electrode samples. For both RuO₂- and IrO₂-coated electrodes, the voltammetric charge and the Zn²⁺ measured area were found to have a linear relationship with oxide loading. The correlation for RuO₂ was found to be 6.2 ± 0.6 C/m², and for IrO₂ it was 3.5 ± 0.5 C/m². The differences in the correlations for the two oxides has been attributed to differences in chlorine content of the two dioxides and consequential differences in grain boundaries and crystal defects.

Low overpotential exchange current densities of the ferric-ferrous couple were measured in concentrated solution (0.5 M Fe²⁺, 0.5 M Fe³⁺, 1 M HCl) at Pt, RuO₂, and IrO₂ RDEs. Significant corrections were necessary for infrared, mass transfer effects, and nonuniform current distribution. The data show that the electrocatalytic activity of RuO₂ ($k_s = 1.92 \times 10^{-3}$ cm/s) is comparable to that of Pt ($k_s = 1.42 \times 10^{-3}$ cm/s) while the activity of IrO₂ ($k_s = 1.21 \times 10^{-4}$ cm/s) is approximately an order of magnitude less than Pt. Since the measured free energy of activation was similar for all three substrates (5.4 - 5.8 kcal/mol), a nonbinding interaction between the couple and the surfaces is suggested (*i.e.*, outer-sphere transfer mechanism). The variation in exchange currents among the different substrates can be attributed to double layer effects and arguments based on crystal differences.

The reaction orders of the ferric-ferrous couple in concentrated chloride solutions appear to be first order. However, measured cathodic and anodic transfer coefficients are 0.30 and 0.25, respectively, for RuO₂ and 0.26 and 0.20, respectively, for IrO₂. This suggests a mechanism other than simple one-step kinetics. Further work is needed to verify and elucidate the meaning of these results.

Regarding the reproducibility of the metal oxide coatings, IrO₂ appears to be more stable than RuO₂. Also, the kinetic data at the IrO₂ surfaces were found to be more reproducible. In evaluating porous electrode theory by experiment, a very reproducible electrode surface is desirable so that kinetic rate expressions can be used with confidence. Consequently, it appears as though the IrO₂ coating is a more promising candidate for this application.

Avenues for further research in 1983 are suggested and include the following:

- Redox reactions have high exchange current densities; consequently, the current distribution at the disk is very nonuniform. Improved

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

SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025 (U.S.A.)

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