

It was found that organic metallic compounds can be utilized as electrodes in aqueous media. Their use as electrodes in electroanalytical techniques or in other electrochemical devices may be possible. In addition, the formation of a variety of insoluble compounds on the electrode surface may be of interest.

Acknowledgments

The support of The Electrochemical Society through the Edward Weston Fellowship is gratefully acknowledged. In addition, the author wishes to thank Dr. Allen J. Bard for his support and guidance and Dr. William L. Wallace for his valuable assistance.

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The Colin Garfield Fink Summer Fellowship Report

Mr. Wilhelm's report is given below.

Electron Injection from Semiconductor Electrodes in Liquid Ammonia

The electrochemical generation of solvated electrons (e^-_s) can be observed in solvents capable of dissolving alkali metals (1). A blue coloration around the cathode at highly negative potentials is characteristic of the formation of e^-_s . Recently there has been a considerable interest in the mechanism of electrochemical generation of solvated electrons as a fundamental electrochemical phenomenon (2-6).

In hexamethylphosphoric triamide (HMPA) the generation of e^-_s was found to depend on the state of the electrode surface (2). Also, there was some disagreement as to whether the reaction is diffusion controlled (2, 4). By examination of this reaction in liquid NH_3 it was hoped that the complication of surface effects could be avoided. Also correlation of kinetic data with known physical properties of e^-_s is facilitated by the fact that solvated electrons have been extensively studied in this solvent (7). In this investigation the injection of solvated electrons was studied at narrow bandgap semiconductors (n,p-Ge, GaAs) in liquid NH_3 in order to examine the mechanism of the generation process with respect to the electronic structure of the electrode and the state of the electrode surface.

Experimental

A three-compartment cell similar in design to that of Demortier and Bard (8) was used. The cell incorporated four electrodes. The counter-(Pt gauze) and reference (Ag wire) electrodes were separated from the main compartment by fine glass Feits. Silver nitrate was added to the reference compartment and all potentials are reported vs. Ag/Ag^+ (0.01M). The working electrode was either a Pt wire or a single crystal semiconductor. The method of preparation of the semiconductor electrodes has been described previously (9). The composition and properties of the single crystal semiconductors are summarized in Table I. Each semiconductor electrode was etched in a solution of 1M $HCl + 0.01M HF$ prior to use.

In a typical experiment, dry KI was placed in the cell along with a Pyrex-covered stirring bar. The cell was evacuated (10^{-5} Torr) and heated ($300^\circ C$) for several hours. $NH_3(g)$ was trapped over a piece of clean Na to remove traces of H_2O and O_2 before vacuum transfer to the cell. The resulting solution was 2 mole percent (m/o) in KI. The cell was thermostated at $205^\circ \pm 1^\circ K$ ($-68^\circ C$) throughout all experiments. Current-voltage curves were obtained by scanning the electrode potential in a cathodic direction at 1 mV/sec. The solution resistance was compensated with positive feedback. In certain experiments the electrodes were illuminated with polychromatic light ($400 < \lambda < 900$ nm) from a 250W tungsten lamp.

Results and Discussion

Polarization curves are shown in Fig. 1 and 2. The anodic reaction is iodide ion discharge. Illumination of the n-type semiconductor electrodes (Fig. 1) reduces the potential necessary for the oxidation reaction below that for nonilluminated electrodes. The overpotential remains greater than that for Pt.

The cathodic reaction is generation of solvated electrons (e^-_s)



where e^-_m is an electron in a metal or semiconductor. In liquid NH_3 and HMPA the generation is a primary process. It does not involve reduction and subsequent dissolution of alkali metal cations. During the cathodic reaction a uniform blue coloration is observed at the

Table I. Compositions and properties of single crystal semiconductors

Semiconductor	E_g (eV)	Orientation	Dopant	Ohmic contact	N_D^*	V^{+FB} V vs. Ag/Ag^+	Dielectric constant ϵ
n-Ge	0.66	<100>	As $10^{18}/cm^3$	In	10^{18}	-0.40	15.8
p-Ge	0.66	<100>	Hg $10^{14}/cm^3$	In/ Δ	10^{14}	-0.25	15.8
n-GaAs	1.35	<100>	Te $10^{17}/cm^3$	In/Au/ Δ	10^{17}	+0.25	13.1
p-GaAs	1.35	<111>	Zn $10^{19}/cm^3$	Au	10^{19}	+0.15	13.1

* From Mott-Schottky plots.

Δ From photocurrent measurements.

Δ Heated in H_2 atmosphere ($300^\circ C$).

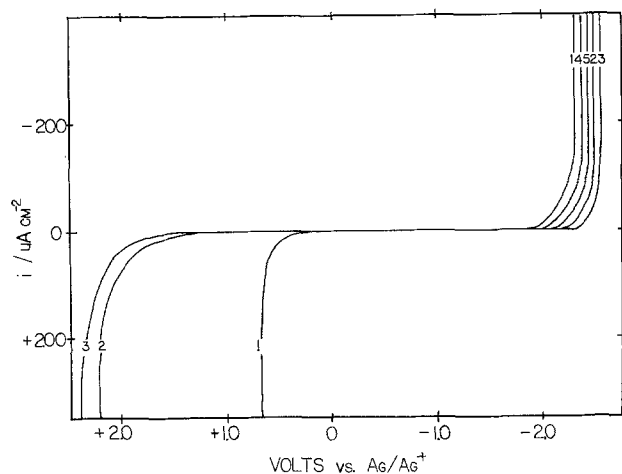


Fig. 1. Polarization curves for p-type semiconductors: 1, Pt; 2, p-GaAs; 3, p-Ge; 4, p-GaAs illuminated; 5, p-Ge illuminated.

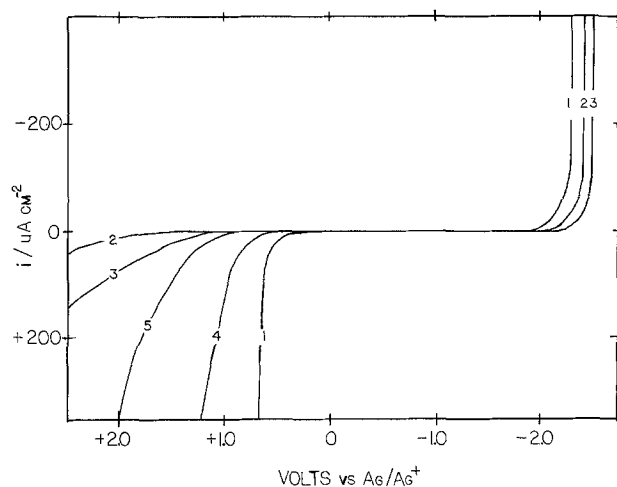
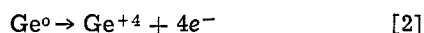


Fig. 2. Polarization curves for n-type semiconductors: 1, Pt; 2, n-GaAs; 3, n-Ge; 4, n-GaAs illuminated; 5, n-Ge illuminated.

electrode surfaces which is characteristic of e^-_s . Illumination of the p-type materials slightly decreases (150 mV) the potential necessary for electron injection. The effect of illumination at visible wavelengths is primarily photovoltaic. The kinetics of the reaction (*i.e.*, the Tafel curves, Fig. 3) remain unchanged with and without illumination.

The potential of the initial appearance of the cathodic reaction is not highly reproducible at the semiconductor electrodes. It depends on the preparation and state of the surface to some extent. Figures 1 and 2 demonstrate the i - E behavior corresponding to the initial scan of a freshly etched electrode. In subsequent scans, the curves shifted cathodically, 25–30 mV.

Only the n-Ge electrode shows semireversible behavior toward oxidation of e^-_s (Fig. 4). The back-reaction could not be observed at p-Ge, p-GaAs, or n-GaAs. Repeated cyclic scanning of n-Ge caused the anodic peak (Fig. 4) to decrease in magnitude, finally disappearing completely after 3 or 4 scans (0.5 V/sec). The oxidative capability could be regenerated by strong anodic polarization (+3.0V, 30–60 sec). The anodic treatment generated a fresh electrode surface by Ge dissolution



At scan rates of less than 50 mV/sec the anodic peak (–2.3V, n-Ge, Fig. 4) could not be observed. This suggests that cathodic polarization or e^-_s as a solution species may induce film formation on the electrode surface. A similar effect is observed in HMPA: The composition of such a passivating film (if any) is not

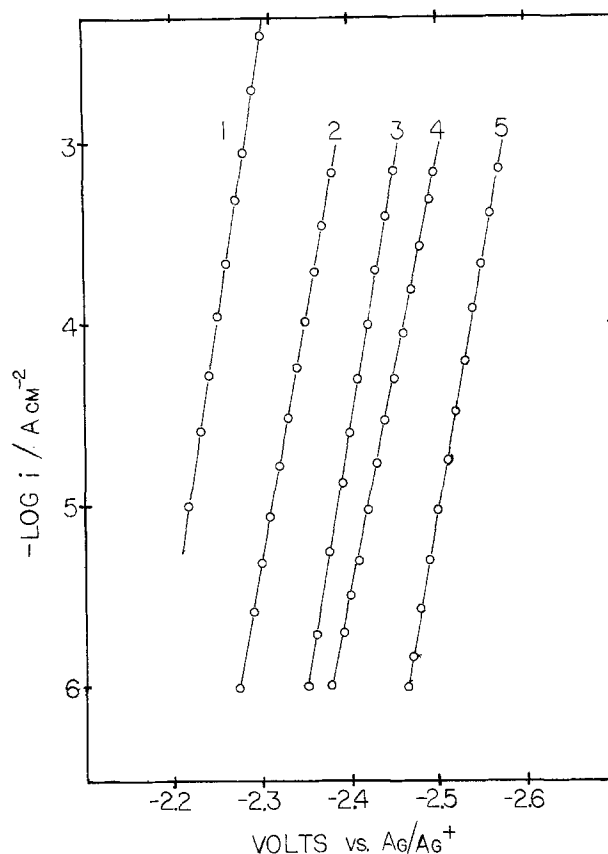


Fig. 3. Tafel plots: 1, Pt; 2, n-GaAs; 3, p-GaAs; 4, n-Ge; 5, p-Ge, scan rate 1 mV/sec cathodic.

known. In HMPA it is attributed to solvent decomposition products or alkali metal hydroxides. Close inspection of the semiconductor electrodes after removal from the cell did not reveal any noticeable change in the electrode surface.

Tafel plots ($\log i$ vs. E) are shown in Fig. 3. The slopes for the semiconductor electrodes and for a Pt electrode are essentially equal (Table II). This equivalency and the relatively close proximity of the potentials of electron injection for both p- and n-type materials suggest that the semiconductors exhibit metal-like behavior (degeneracy) in this potential range. Under these conditions the entire voltage drop is in the Helmholtz layer and the i - E relationship is analogous to that for metals

$$i = i_0 \left[\exp \left(\frac{-\alpha F n}{RT} \right) - \exp \left(\frac{-\beta F n}{RT} \right) \right] \quad [3]$$

with transfer coefficients (α, β) equaling 1 and 0, respectively.

In a report published while this investigation was in progress (6), the cyclic voltammetric behavior of e^-_s at Pt electrodes was found to be diffusion controlled. A Tafel slope of RT/F could be predicted by assuming that diffusion of reactant to the electrode was not a factor and that the electrode process was governed by the Nernst equation. Although the latter criterion does not

Table II. Kinetic data from Tafel plots (Fig. 3) 7–205°K

Electrode	Slope (mV/decade)	α
Pt	36	1.13
n-Ge	41	0.99
p-Ge	37	1.10
n-GaAs	38	1.07
p-GaAs	35	1.16

The Joseph W. Richards Summer Fellowship Report

Ms. Novak's report is given below.

Cl⁻ Ion and Oxide Film Coverage Effects in Anodic Cl₂ Evolution Kinetics

In recent years, particular attention has been given to the study of the behavior of various noble metal and noble metal oxide surfaces which are currently being used as electrocatalyst surfaces for commercial electrochemical Cl₂ production (1-3). Special attention has been given to the preparation of oxidized metal anodes, such as RuO₂, which could be used also with a Ti/TiO₂ substrate in so-called DSA electrodes (2-4).

Chlorine evolution kinetics has been studied by a number of authors (5-8), mostly using noble metal electrodes such as Pt, Ir, and Rh. Agreement on the kinetics of the pathways of the over-all reaction, its mechanism, and the influence of the oxide film which normally exists on noble metal surfaces operating as anodes for Cl₂ evolution in aqueous medium has not yet been reached. In a previous study by Yokoyama and Enyo (9), it was concluded that the rate-controlling process in the anodic direction is the Cl⁻ ion-discharge step followed by a fast Cl· recombination step. Krishtalik *et al.* (10) proposed a so-called "chloronium" ion (Cl⁺) mechanism, based on the study of the Cl₂ evolution process on RuO₂ anodes. This mechanism involved formation of Cl₃⁻ together with Cl· and Cl⁺ as intermediates on the metal anode surface. The influence of the oxide surface film at the anode surface on the Cl₂ evolution process was discussed by Arikado *et al.* (11); although the current densities at different potentials were related to the d-band vacancies and different oxide coverage of the Pt and Pt alloy surfaces which these authors used, these effects were not explained in terms of the over-all mechanism of the Cl₂ evolution reaction and its consecutive steps. Littauer and Shreir (12) recognized the significance of the oxide film present at Pt anodes in Cl₂ evolution but the state of the film and its coverage were not characterized.

In aqueous media, Cl₂ evolution proceeds on an oxidized or partially oxidized surface of the anode metal since most metal surfaces are already oxidized at potentials below, or close to, the Cl₂ reversible potential. This would suggest that it is the properties of the surface oxide film on the metal anode that are of greater importance for the Cl₂ evolution reaction than the properties of the bare metal surface itself. It was therefore decided to compare the electrocatalytic behavior of an unoxidized Pt anode surface which can be obtained in anhydrous trifluoroacetic acid (TFA) with RbCl as electrolyte, with that of an oxidized Pt electrode surface in regular aqueous KCl solutions. In both solvent media, as well as in TFA/H₂O mixtures, when the water content in the solutions was changed from 0 to 100% H₂O, the same type of current-potential behavior was observed, *viz.* a curved Tafel relation with an approach to a limiting current as electrode potential was increased, suggesting a recombination-controlled (2Cl·_{ads} → Cl₂) mechanism applying under all conditions so that solvation effects on the state of the Cl⁻ ion reactant are only secondary. In order to establish that the limiting current densities were not due to Cl⁻ ion diffusion control, experiments were carried out at a rotating disk electrode at various rotation rates, ω . The limiting current densities were independent of ω (0-6400 rpm) and were also not due to ohmic (iR) resistance effects.

In the TFA/water mixtures a steady increase in the limiting current densities was observed as the water content of the solutions was changed from almost zero mole fraction (completely dry solution) to a mole fraction of 1 (fully aqueous solution) where an oxide film

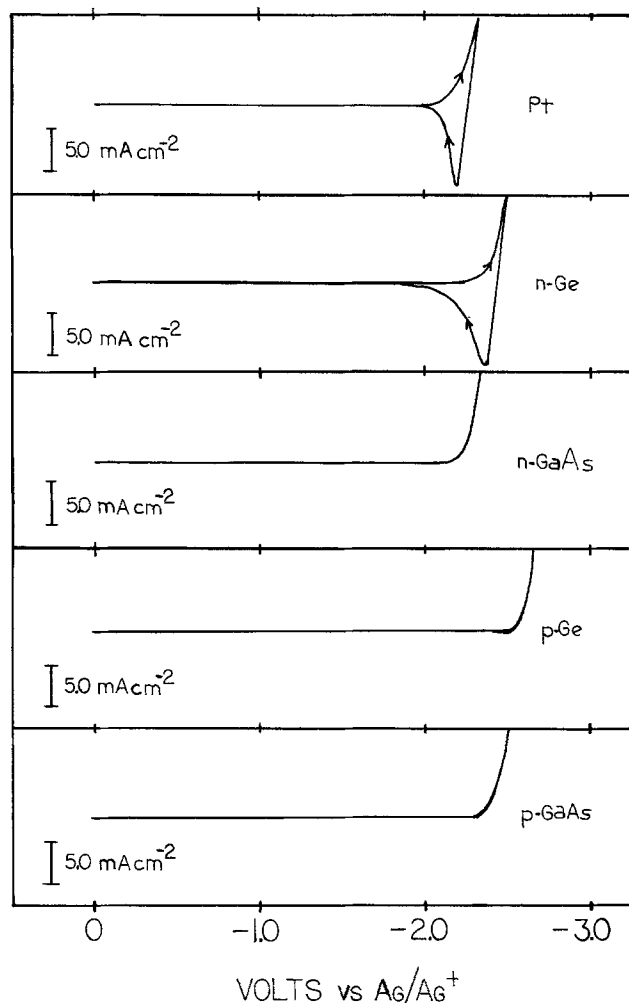


Fig. 4. Cyclic voltammetry, scan rate 500 mV/sec

hold for n-GaAs, p-Ge, and p-GaAs for which no oxidative capability was observed, all of the semiconductor electrodes exhibited a pronounced sensitivity to stirring of the solution during cathodic scans. The uniform kinetic behavior of n- and p-type materials with or without illumination also suggests that the cathodic generation of e⁻_s is not activation controlled at semiconductor electrodes in liquid ammonia.

Acknowledgments

The support of the Electrochemical Society through the Colin Garfield Fink Fellowship and consultations of Professor Norman Hackerman are gratefully acknowledged.

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