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HYDROGEN EVOLUTION FROM KHF_2
MELTS AT PLATINUM ELECTRODES

by

G. B. BARBI, S. PIZZINI, G. STERNHEIM

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Joint Nuclear Research Centre
Ispra Establishment (Italy)
Materials Department

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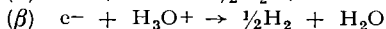
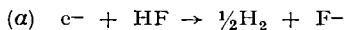
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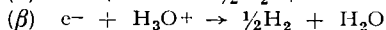
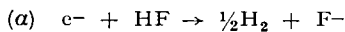
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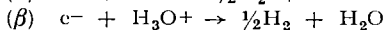
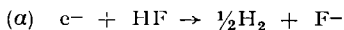
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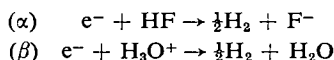
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HYDROGEN EVOLUTION FROM KHF_2 MELTS AT PLATINUM ELECTRODES*

S. PIZZINI, G. STERNHEIM and G. B. BARBI
Laboratory for High Temperature Chemistry, Materials Department,
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Abstract—Overvoltage measurements at bright platinum electrodes have been carried out, by the galvanostatic method, in order to investigate the hydrogen evolution reaction from molten KHF_2 baths containing different amounts of water in solution.

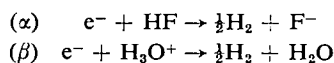
The equations



are attributed to the observed electrode reactions. In the region of current density corresponding to the transition from reaction (α) to (β), the electrode is treated as a bi-electrode.

Résumé—Des mesures de surtension sur des électrodes en platine poli ont été effectuées par le méthode galvanostatique, dans le but d'étudier les réactions de production d'hydrogène à partir de bains de KHF_2 fondu contenant en solution des quantités variables d'eau.

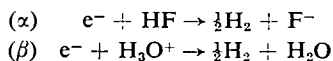
Les équations



ont été attribuées aux réactions d'électrode observées. Dans la région de densité de courant correspondant à la transition de la réaction (α) à (β), l'électrode a été traitée comme une bi-électrode.

Zusammenfassung—Überspannungsmessungen wurden an glatten Platin-Elektroden nach der galvanostatischen Methode ausgeführt, um die Wasserstoffentwicklungs-Reaktion in Schmelzen von KHF_2 mit variablen Mengen Wasser, zu untersuchen.

Die Elektrodenreaktionen wurden durch die folgenden Reaktionen beschrieben:

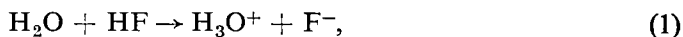


In dem Bereich der Stromdichte, in welchem der Uebergang von Reaktion (α) zu (β) liegt, wurde die Elektrode als Zweifache-Elektrode angesehen.

INTRODUCTION

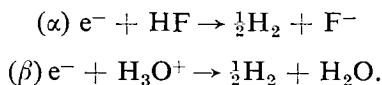
OVERVOLTAGE measurements have been carried out in order to investigate the hydrogen evolution reaction in molten KHF_2 baths at bright platinum electrodes. Variable amounts of water have been added to the melt in quantities ranging from 0.1 to 1.8 wt. %.

Hydrogen fluoride being strongly acidic, the water in the melt is supposed to act as a proton acceptor, according to the reaction



which accounts for the extremely low thermodynamic activity of water in such melts.¹

From the overvoltage current-density curves (Fig. 1) it can be noted that the evolution of hydrogen occurs according to two different electrode reactions.



* Manuscript received 12 July 1962.

There is a region of current density corresponding to the transition from reaction (α) to (β) where the electrode can be treated as a bi-electrode, equation (1) being the coupling reaction (Binnenreaktion) in solution.²

EXPERIMENTAL

Molten KHF_2 with a variable content of water was prepared by fusion of the salt under a dry atmosphere of nitrogen. A preliminary electrolysis has been carried out by using graphite electrodes, to deposit trace amounts of impurities. Then a sample was taken for determining the water present in the melt. A modified Karl Fischer method was used, as described elsewhere.³

All experiments were carried out at 250°C . Overvoltage measurements were carried out by the galvanostatic method. Voltage responses across the tensiometric cell were recorded both by a Leeds & Northrup potentiometric recorder and Tektronix cathodic ray oscillograph. An electrometric d.c. amplifier was inserted. Electrode and counter-electrode were arranged in cylindrical symmetry.

The reference electrode was an iso-electrode probe⁴ whose reaction is (α) (Fig. 2b). It attains equilibrium very rapidly; it is reproducible to less than 1 mV. Teflon was used as insulating material.

RESULTS

The stationary values of overvoltage as a function of current density are plotted in Fig. 1, for several different water concentrations.

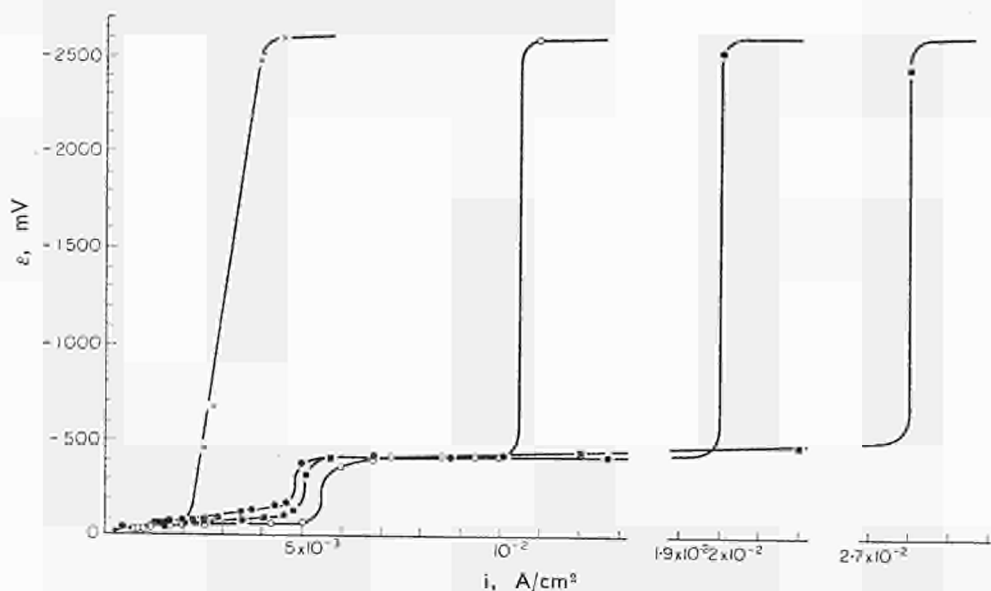


FIG. 1. ϵ vs. i plot for different water contents in a molten KHF_2 bath. $T = 250^\circ\text{C}$, Platinum electrode. Cathodic hydrogen evolution.

- × 0.01% wt. H_2O
- 0.135% wt. H_2O
- 0.20% wt. H_2O
- 0.34% wt. H_2O

There is evidence that the first limiting current corresponding to the transition from one reaction to the other of the two hydrogen evolving steps is practically constant, i.e. independent of water concentration.

Figure 3 is a plot of the second limiting current vs. water content in the melt. The slope of the straight line corresponds to a value D/δ of about 5×10^{-4} cm/sec, where D is the diffusion coefficient (cm^2/sec) of H_3O^+ and δ the thickness (cm) of the diffusion layer.

Voltage vs. time responses are shown in Fig. 4; typical recorded diagrams are given for different regions of current density. In particular, Fig. 4(b) illustrates the

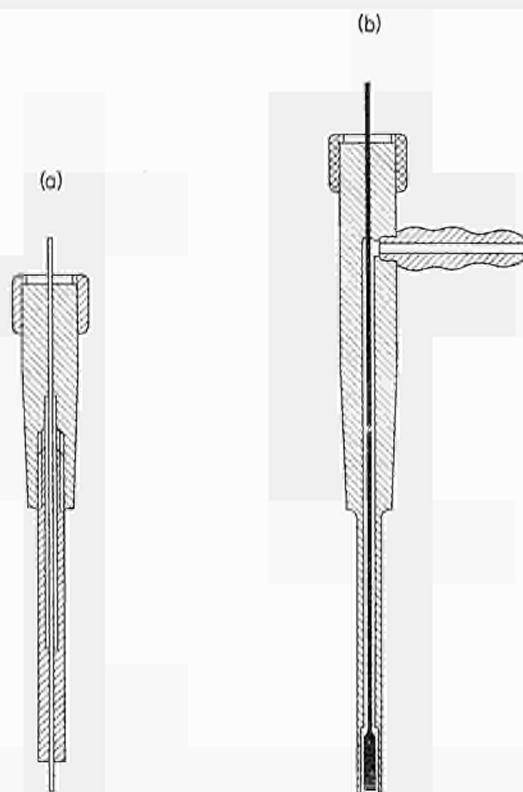


FIG. 2. (a) Platinum electrode. (b) Hydrogen reference electrode.
All insulating parts made of Teflon.

behaviour of the electrode at current densities between the two limiting currents mentioned.

It is interesting to note that when the current is interrupted, the voltage attains its rest value only after a certain time, dependent upon the total quantity of electricity passed and upon the surface conditions of the electrode. A voltage plateau is developed, the value of which is practically constant for all water concentrations and current densities. From this value the voltage falls to its rest value, passing through an inflexion.

This inflexion is no longer observed when the current density exceeds the second limiting current and the polarization of the electrode attains a voltage comparable to that of the discharge of potassium. At open circuit the voltage then falls rapidly to its rest value.

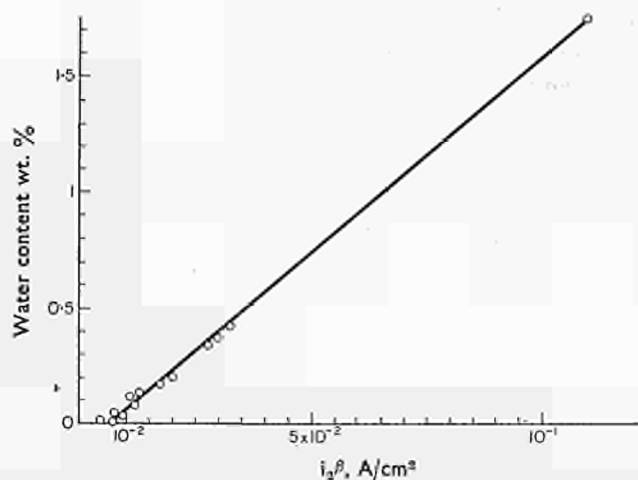


FIG. 3. Limiting currents for the (β) reactions vs. water content of the KHF_2 melt. $T = 250^\circ\text{C}$.

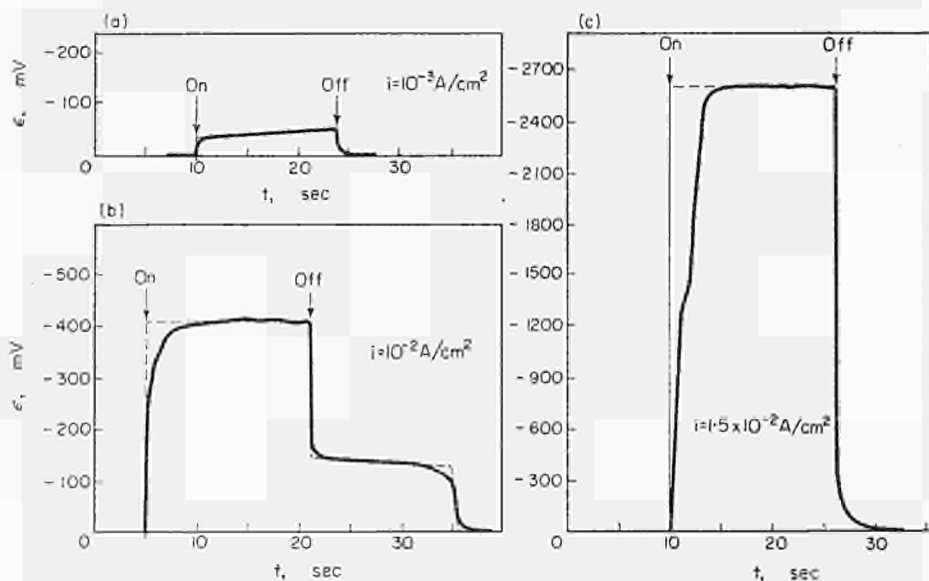
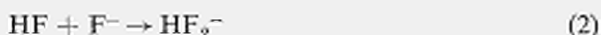


FIG. 4. E vs. t response at various current densities. (a) Region of the (α) reaction. (b) Region of the (β) reaction. (c) Potassium discharge. $T = 250^\circ\text{C}$, $C_{\text{H}_2\text{O}} = 0.13$ wt. %.

DISCUSSION

Considering that reaction (1) is strongly shifted to the right, we consider reaction (β) to be the only one possible to account for the behaviour of the electrode in the intermediate region of current densities.

Hydrogen fluoride is strongly associated in difluoride melts, according to the reaction



We have postulated that the discharge of HF according to the reaction (α) corresponds to the reaction occurring at low current densities.

The discharge of hydrogen from HF_2^- is shifted to much more negative values due to the high affinity of reaction (2).

For the electrode reactions (α) and (β) the following relations exist:

$$E_\alpha = E_\alpha^\circ + \frac{RT}{F} \ln \frac{a_{\text{HF}}}{a_{\text{F}^-} p_{\text{H}_2}^{1/2}} = E_\alpha^{\prime\circ} + \frac{RT}{F} \ln \frac{a_{\text{HF}}}{a_{\text{F}^-}}, \quad (3)$$

$$E_\beta = E_\beta^\circ + \frac{RT}{F} \ln \frac{a_{\text{H}_3\text{O}^+}}{a_{\text{H}_2\text{O}} p_{\text{H}_2}^{1/2}} = E_\beta^{\prime\circ} + \frac{RT}{F} \ln \frac{a_{\text{H}_3\text{O}^+}}{a_{\text{H}_2\text{O}}}. \quad (4)$$

For a bi-electrode (α) (β) at equilibrium, we have

$$E_\alpha = E_\beta, \quad (5)$$

and, at the point of equivalence, i.e. if

$$\frac{a_{\text{HF}}}{a_{\text{F}^-}} = \frac{a_{\text{H}_2\text{O}}}{a_{\text{H}_3\text{O}^+}}, \quad (6)$$

we have

$$E_{\text{cql}} = \frac{1}{2}(E_\alpha^{\prime\circ} + E_\beta^{\prime\circ}). \quad (7)$$

The standard free enthalpy of reaction (1) is given by

$$-\Delta G^\circ = RT \ln K = F(E_\beta^{\prime\circ} - E_\alpha^{\prime\circ}), \quad (8)$$

where

$$K = \frac{a_{\text{H}_3\text{O}^+} a_{\text{F}^-}}{a_{\text{H}_2\text{O}} a_{\text{HF}}}. \quad (9)$$

To calculate $(E_\beta^{\prime\circ} - E_\alpha^{\prime\circ})$ we used the diagram² shown in Fig. 5. The assumption is made that the point of neutrality can be evaluated by taking the half-wave potential of the inflexion ($\varepsilon_{\text{cql}}^{\text{ref}} = -65$ mV) which appears at open circuit when the electrode has been working in the (β) range. In Fig. 5 we plot the functions (3) and (4) vs. $\ln a_{\text{HF}}/a_{\text{F}^-}$ and $\ln a_{\text{H}_2\text{O}}/a_{\text{H}_3\text{O}^+}$, respectively. We take as a reference $E_\alpha^{\prime\circ} = 0$.

Thus our reference electrode, which is an (α) electrode, takes the voltage

$$E_\alpha = + \frac{RT}{F} \ln p_{\text{HF}}$$

$$(p_{\text{HF}} = 39.8 \text{ mm Hg. } E_\alpha = -133 \text{ mV}).$$

We have

$$E_{\text{cql}} = \varepsilon_{\text{cql}}^{\text{ref}} + E_\alpha = -198 \text{ mV}$$

and from (7)

$$E_\beta^{\prime\circ} = -396 \text{ mV.}$$

The free enthalpy of reaction (1) will be

$$\Delta G = -9135 \text{ cal/mole}$$

and

$$\log_{10} K = 3.83.$$

Of course, this evaluation of the free enthalpy of reaction (I) is based on the assumption that the electrode is at equilibrium with respect to both (α) and (β) redox couples.

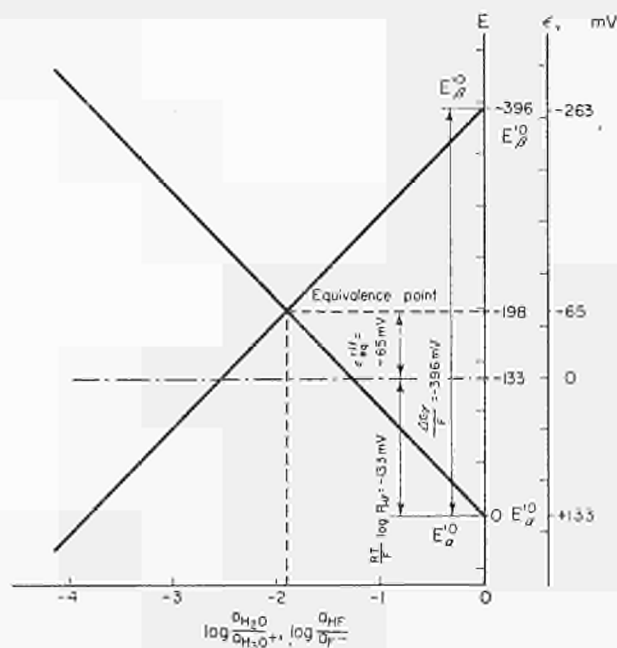


FIG. 5. Equilibrium values of voltage for the (α) and (β) electrode reactions on the basis of the experimental determination of the equivalence point.

Overtension contributions dependent upon activation of the reactions and modifications of the electrode surface deserve a further investigation; they will be dealt with in a subsequent paper.

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