The cathodic hydrogen evolution reaction at the tin electrode in molten organic salt

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Dedicated to Associate Professor K. Matiašovský, DrSc., in honour of his 60th birthday

The hydrogen evolution reaction in pure molten triethylammonium fluoroborate at the bare tin electrode has been investigated by the galvanostatic method. It was found that the reaction is much faster than in acidic aqueous solutions. The catalytic effect was attributed to the behaviour of the amine molecules which were present in a molten alkylammonium salt.

The hydrogen electrode reaction (h.e.r.) is the most studied electrode process, because it is the only case in which the kinetics can be observed on most of the metals except the alkali and alkali earth metals. The cathodic hydrogen evolution at metallic electrodes in aqueous solutions has been studied by many authors [1—4] in order to find the correlation between electroactivity of metals in the h.e.r. and their electronic configuration.

In our studies the h.e.r. was carried out in molten alkylammonium salts. In this work we have chosen molten triethylammonium fluoroborate ($TEABF_4$) as a solvent, because the concentration of H^+ ions in this molten salt as well as the basic physicochemical properties were known [5—9].

The change of solvent from water to the molten alkylammonium salt manifests itself by the following main features: the higher temperature at which the reaction occurs, the different concentration of H^+ ions, the much higher ionic strength. In our previous papers [10—13] the h.e.r. was studied in this solvent using various metals of the sixth long period and Ib, IIb, and IIIa groups. This paper presents the results obtained at the bare tin electrode in the same solvent.

Experimental

$TEABF_4$ has been obtained by the reaction of triethylamine with HBF_4. The salt was recrystallized twice from butyl alcohol and then dried *in vacuo* at 100 °C for 6 h. The indicator tin electrode had a shape of a rod sealed in a glass pipe. It was made of anal. grade metal (POCH, Gliwice). Its geometrical surface was about 0.1 cm^2 The auxiliary

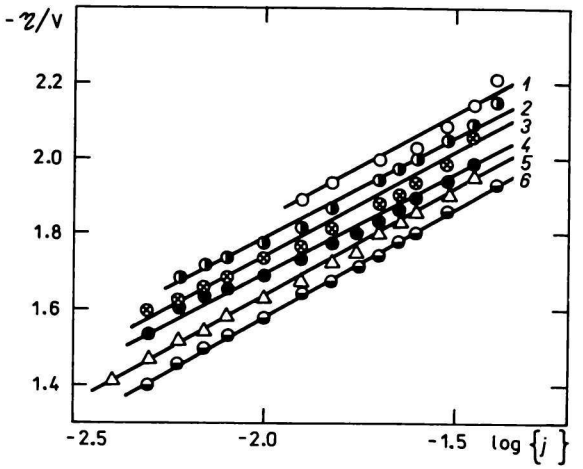

Fig. 1. Plots of the electrode overpotential η against log of the current density for the Sn electrode in molten $TEABF_4$ at various temperatures T/K: *1.* 403, *2.* 413, *3.* 423, *4.* 433, *5.* 443, *6.* 453.

Table 1

The kinetic parameters of the h.e.r. at the Sn electrode in molten $TEABF_4$

T/K	j_0/(A cm^{-2})	α_c	$U^{\ddagger}$/(kJ mol^{-1})
403	3.77×10^{-6}	0.15	49 ± 7
413	5.30×10^{-6}	0.15	
423	9.28×10^{-6}	0.15	
433	7.66×10^{-6}	0.16	
443	1.40×10^{-5}	0.15	
453	2.12×10^{-5}	0.15	

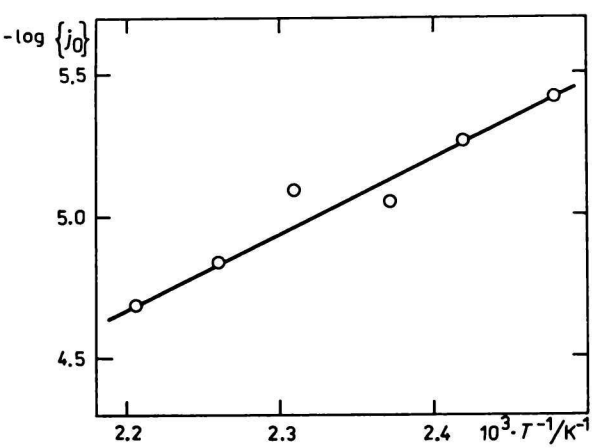

Fig. 2. Temperature dependence of log of the exchange current density of the h.e.r. at the Sn electrode.

electrode was a rod made of a glassy carbon. The reference electrode was the hydrogen electrode immersed directly in the pure fused salt. Auxiliary as well as the reference electrode was placed in a separate compartment with a glass filter. The measuring cell and circuit was described earlier [14]. The measurements were carried out in nitrogen atmosphere.

Results and discussion

The h.e.r. at the Sn electrode in molten $TEABF_4$ was studied by the galvanostatic method. The overpotential *vs.* time plots were recorded at different current densities from 5×10^{-3} to 5×10^{-2} A cm^{-2} in the temperature range 403—453 K. The polarization curves and Tafel plots were obtained by the Berzins—Delahay method [15, 16] as it was shown earlier [14]. The exchange current densities j_0 and the overall cathodic transfer coefficient α_c obtained from Tafel plots (Fig. 1) by the least-squares method are presented in Table 1.

The temperature dependence of the exchange current densities presented in Fig. 2 was used for calculating the overall apparent activation energy $U^{\neq}$ of the h.e.r. It is evident that the exchange current density of the h.e.r. at the Sn electrode in pure molten $TEABF_4$ is about five orders of magnitude higher than in 1 M acidic aqueous solution [3] although the concentration of H^+ ions in molten $TEABF_4$ at 403 K is 10^3 times lower. Similar differences were observed at Pb and the other metals *sp* examined in this molten salt [11—13].

This catalytic effect can be due to the amine molecules which appear in the molten salt as a result of ionization of the alkylammonium cations. The amine molecules are well adsorbed on the electrode surface owing to their lone electron pair. On the other hand, they are in equilibrium with alkylammonium cations, which discharge on the electrode surface to the BH radicals, and two such radicals recombine to form 2B and H_2. This mechanism of catalytic activity of some organic compounds having the lone electron pair was proposed earlier by *Mairanovskii* [17].

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