Cathodic H_2 Evolution from Molten HF, H_2O and H_3O^+ Solvates, and the Nature of the Catalytic Surface for H_2 Formation

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The cathodic H_2 evolution reaction (the HER) has been studied primarily from aqueous solutions though significant works have reported results on the kinetics of the HER from alcoholic [1] and some other [2] solvents with the purpose of examining proton solvation effects in the initial discharge step [1,2] and the role of proton-tunneling [3] in that step. On the other hand, rather little work has been done on studies of the HER from proton sources at low activity, e.g. in KF·2HF and its aqueous analogue, K or NaOH·2H_2O. In the former case the anion is FHF^- with solvation of K^+ and the F^- anion by the second HF molecule. In NaOH·2H_2O, the speciation of hydrated ions is less clear, although Na^+H_2O and HO--H--OH^- or HO^---H--OH anions are the probable species.

In the present work, kinetic polarization relations have been determined for the HER from KF·2HF and NaOH·2H_2O molten solvates in comparison with kinetics of the HER in dilute alkaline solutions. The cathode materials are stainless-steel and Monel as used in the practice of electrolytic F_2 generation from KF·2HF electrolytes. Polycrystalline Pt was also examined comparatively as a cathode for the HER from the solvates since, at that metal, the H underpotential deposition behavior can also be determined and thus the catalytic surface (see below) on which the HER proceeds identified (cf. ref.4).

Cathodic H_2 evolution from molten (85^oC) KF·2HF exhibits some unusual features in that "hyperpolarization" of the cathode can set in at elevated current-densities, depending on prior conditions of time and magnitude of currents passed. Formally, this effect appears analogous to the well known "anode effect" encountered at C anodes used for anodic F_2 generation. However, the origins of the "cathodic" seems different from those for the "anodic effect". If the electrolysis is conducted near the m.p. of KF·2HF, hyperpolarization can set in at the cathode owing to local onset of solidification of the melt in the diffusion layer. This effect can be eliminated by rotation of the electrode having a conical surface and/or by ultrosonication which then disperses the tendency for local solidification. However, an additional effect also arises, like it does at C anodes in KF melts, due to difficulty of H_2 bubble detachment. This effect is found to be promoted by the presence of As-species (AsF_3 or AsF_4^-) in the melt at low concentrations which induces large changes of the contact-angle of the bubble with the metal electrode surface as measured telescopically by means of a contact-angle goniometer.

The kinetic solvate effects led us to examine related behaviour that can be studied with solvates of H^+ in the molten $CF_3SO_3·H_3O^+$ acid-salt, through other solvates $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ through to dilute aqueous $CF_3SO_3^-/H_3O^+$ solutions. These hydrates were also studied by means of differential capacitance measurements at Hg.

The effects referred to in all the preceding paragraphs originate in ways connected with the properties of the electrolyte or solvent used [1,2] for study of the HER.

However, other effects of equal and complementary importance arise with regard to the state and nature of the cathode metal surface at which protons are discharged , H atoms are chemisorbed and molecular H_2 formation takes place. At the catalytic noble metals, Pt, Rh, Pd, Ru, the highest exchange current-densities, i_o, for the HER arise so that these metals appear at or near the apex of the volcano-curve [5] that can be plotted [6] in terms of log i_o vs. metal-to-H bond energy or, on a theoretical basis [5], log i_o vs. standard Gibbs energy of chemisorption of 2H from H_2. The form of the volcano relation for the HER was, at first, interpreted in terms of the energies of direct bonding of H to the electrocatalyst metal surface. However, Conway and Tilak pointed out in 1992 (pp.76-77 and p.51 in ref.7) that the most active noble metals, as above, were fully covered by chemisorbed (under potential-deposited) H already at the H_2/H^+ reversible potential, so that any relation of HER kinetics to H binding energy to the metal should be that to the (weaker) binding energy of the *extra overpotential-deposited* (OPD) H intermediate (beyond, and codeposited on or with the full UPD layer) involved kinetically in the steps of the HER. In this way, it can be understood how the Tafel slope of 2.3RT/2F can arise for the HER on Pt yet the overall H coverage, θ_H, is formally greater than a monolayer. This difficulty, previously unresolved, led also to the possibility that the 2.3RT/2F value was a pseudo-Tafel slope due to H_2 diffusion effects arising from H_2 supersaturation in a diffusion layer.

The above features of the kinetics of the HER, e.g. at Pt, require reinterpretation of the volcano curve in the way treated more quantitatively by Conway and Jerkiewicz in ref.4. Thus, the states of the surface of metals that are most catalytically active for the HER should be Pt/H ($\theta_{H,UPD} \rightarrow 1$) on which extra OPD H is deposited with coverages related to overpotential and the H (OPD) desorption mechanism. Hence, in terms of mechanisms of the HER at various metals and from various proton-donors it is the OPD H that is of critical importance and of kinetic significance. For the less strongly adsorptive metals, e.g. Au, Ag, Ni, where the coverage fraction, θ_H, is substantially <1, UPD H $\theta << 1$, the UPD species becomes indistinguishable from the OPD species as θ_H increases beyond the reversible H_2 potential. Data for OPD H coverage at Ni and Ni-Mo alloys as f (potential) can be derived and θ (UPD H) is <1 and is not reliably measurable, if at all (cf. ref.8).

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