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SHORT COMMUNICATIONS

KINETICS OF ELECTROCHEMICAL HYDROGEN EVOLUTION AND DISSOLUTION ON GRAPHITE IN MOLTEN $KHSO_4$*

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Although the electrochemical evolution of hydrogen on graphite in bisulphate melts has been studied under a limited range of experimental conditions,[1] no data have been reported about the anodic oxidation of hydrogen in molten electrolytes. An investigation of these reactions was attempted by employing spectroscopic grade graphite and molten potassium bisulphate in the temperature range 230–280°C.

Cathodic potentiostatic and galvanostatic cd/voltage curves were coincident. Good Tafel lines were obtained over the cd range of 9×10^{-5} A/cm² to 15×10^{-3} A/cm². However, the Tafel slopes, $(b)_{T,c}$, were lower with either fresh or recently polished electrodes approaching after successive runs, values close to RT/F. At *ca* 10^{-1} A/cm², a tendency to an infinite slope was exhibited. The cd/voltage characteristic obtained with a vibrating graphite electrode presented similar features. Parameters deduced from the cathodic Tafel lines are assembled in Table 1. The cd extrapolated to zero overvoltage, i_0, was between $33{\cdot}1 \times 10^{-6}$ and 276×10^{-6} A/cm²; from its temperature dependence, an experimental activation energy of about 29 ± 5 Kcal/mole was calculated.

Table 1. Kinetic parameters derived from cathodic Tafel lines

Temp °C	$(b)_{T,c}$ V	$i_0 \times 10^6$ A/cm²	$2{\cdot}303\ RT/F$ V
230	0·076	28·8	0·095
245	0·086	57·5	0·098
261	0·096	120·1	0·101
277	0·104	276·0	0·105

The cathodic overvoltage decay at current interruption was rather slow; it was followed with a potentiometric recorder. The overvoltage decayed logarithmically with time and the decay slopes being between 0·050–0·060 V/decade. The differential electrode capacitances, C_e, obtained from decay curves, decreased with cathodic overvoltage, Table 2.

Anodic cd/voltage curves were always obtained with recently polished graphite

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TABLE 2. DIFFERENTIAL ELECTRODE CAPACITANCES OBTAINED AT CATHODIC OVERVOLTAGES. 277°C

$\eta \times 10^3$ V	$C_s \times 10$ F/cm^2
56	2·31
127	1·63
157	1·57
178	1·44
227	0·70
254	0·37
279	0·26
302	0·15

electrodes. They were characterized by a well defined limiting cd directly proportional to the square root of the hydrogen pressure saturating the melt. The limiting cds obtained at different hydrogen pressures are assembled in Table 3.

The anodic overvoltage decay at current interruption is also a slow process, but no definite simple relationship between overvoltage and time could be established.

TABLE 3. ANODIC LIMITING CURRENTS. 240°C

p_{H_2} atm	$p_{H_2}{}^{1/2}$ atm$^{1/2}$	$i_L \times 10^6$ A/cm^2
0·052	0·228	6·4
0·19	0·44	8·9–12·6
0·27	0·52	14·2–15·9
0·725	0·851	23·7–24·4
1	1	28·2

Although the kinetic parameters of the reaction are well established both for the cathodic as well as the anodic processes, no definite conclusion about the detailed reaction mechanism can yet be deduced. The main conclusion drawn at present is that the hydrogen electrode reactions on graphite in bisulphate melts involve an activated electrochemical reaction, as earlier reported for the reaction occurring on platinum,[2,3] gold[4] and palladium[5] electrodes.

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