Electrode processes on graphite electrodes*

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Since the invention of DSA electrodes for chlorine production in the chlorine-alkali industry, the use of graphite electrodes has declined. At the present time, about 70% of the chlorine produced is formed at graphite electrodes [1]. Two factors are of special interest for chlorine evolution at graphite: the nature and roughness of the graphite electrode surface and the reaction mechanism of chlorine formation.

It is well known [2] that the potential of the graphite anode varies during the evolution of chlorine as a function of the time of anodic polarization. The potential initially rises to a maximum; thereafter it decreases rapidly at first and then gradually until a constant value is reached. The maximum value of the potential during anodic polarization depends on the geometric current density and on the composition of the anolyte [3]. The capacitance $C_p$, determined by the potential static potential jump method, and thus the roughness factor [2], is likewise a function of the time of polarization: the capacitance $C_p$ increases slowly with time until the potential reaches its maximum; with prolonged polarization the capacitance increases rapidly at first and then slowly reaches a constant value at about the same time as the potential becomes constant. The nature of the surface of the graphite anode also depends on the time of anodic polarization [2]. This is clearly demonstrated by the $e/J$ curves determined after several anodic polarization cycles. These curves are represented in Fig. 1. The pronounced change in the $e/J$ curve occurs simultaneously with a marked increase in surface area of the electrode. This ageing process is due to the oxidation of graphite to CO and CO$_2$ and manifests itself in a change in the nature of the graphite electrode and an increase in surface area.

From voltammograms recorded in 4 M NaCl + 1 M HCl solution for highly orientated pyrolytic graphite electrodes, whose edge plane or basal plane served as the electrode surface, and for Acheson graphite electrodes, Janssen [4] has concluded that two different surface compounds, Ip oxygen and hp oxygen, are formed on all these graphite electrodes. In the stationary state, Ip oxygen is present in the potential range of chlorine evolution below about 1250 mV and hp oxygen at potentials higher than about 1350 mV vs SCE. Hine et al. [5] also support this conclusion.

The voltammograms [4] on the electrodes investigated for a potential sweep between about 1100 mV and about 1300 mV are similar to the voltammogram given in Fig. 1 for an electrode which had been charged with 21 Ah/cm$^2$. During chlorine evolution an aged electrode is consequently covered with hp oxygen and/or with chlorine atoms.

Atomic chlorine is adsorbed on the surface of the graphite crystallites [6] during chlorine evolution. The degree of coverage with atomic chlorine is proportional to $Q_c(O)$, i.e. to the quantity of charge required for liberation of all the chlorine present on a graphite anode during the electrolysis. From the experimental relationship between the current density, the potential, and $Q_c(O)$, it clearly appears [7] that for an aged anode the chlorine evolution occurs according to the Volmer/Heyrovsky mechanism, viz.

$$\text{Cl}^- + \text{Cl}_\text{ads} + e^- \rightarrow \text{Cl}_2 \text{ Volmer reaction}$$

$$\text{Cl}^- + \text{Cl}_\text{ads} \rightarrow \text{Cl}_2 + e^- \text{ Heyrovsky reaction}$$

where the Heyrovsky reaction is the rate-determining step. Further, it is established that for an aged electrode in 4 M NaCl + 1 M HCl the ratio between the exchange current density of the Volmer and that of the Heyrovsky reaction is equal to 20, the transfer coefficient of the Heyrovsky reaction is 0.5, the activation energy is 8.4 kcal/mol chlorine, and the degree of coverage with atomic chlorine is 0.05 at the reversible chlorine/chloride electrode potential. Chlorine is also formed according to the Volmer/Heyrovsky mechanism at graphite electrodes whose surface differs from that of an aged electrode; however, the kinetic parameters then depend on the nature of the surface of the graphite anode.

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Fig. 1. Voltammograms on Acheson graphite electrodes which had been polarized with an anodic current density of 30 mA/cm$^2$ in a 4 M NaCl + 1 M HCl solution at 25 °C for different times. The numbers next to the curves indicate the total quantity of charge per cm$^2$ geometric surface area which had been passed through the electrode.

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