BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2264—2265 (1970)

Electrical Properties of the Platinum Anode in a Sodium Chloride Solution

Chiou-Chen Lu, Kazuo Fueki and Takashi Mukaibo

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received February 4, 1970)

In a previous paper[1] the present authors have shown that the anodic overpotential of chlorine evolution at the passivated platinum electrode is about 0.7 V higher than that of the activated electrode at the same current density. The purpose of the present investigation is to determine the electrical resistance, the double-layer capacitance, and the faradaic impedance of the platinum electrode in both active and passive states in a sodium chloride solution, in order to contribute to the elucidation of the passive state.

Experimental and Results

Electrolytic Cell. A platinum wire, 1 mm in diameter, was sealed in a glass tube and then cross-sectioned by grinding with emery paper. The smooth end of the platinum wire was used as the test electrode. The area of the test electrode was 0.008 cm^2. The reference electrode was a platinized platinum ring placed around the test electrode and worked as a reversible chlorine electrode. The counter electrode was a platinum plate of 8 cm^2. During the run, the solution was saturated with chlorine (1 atm).

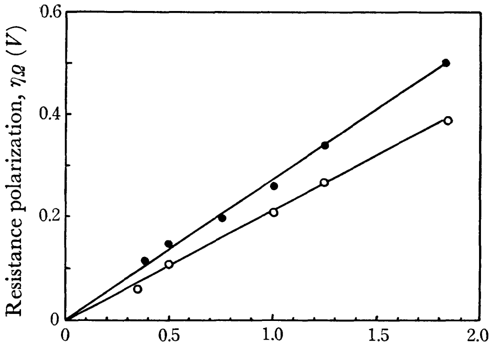


Fig. 1. Resistance polarization *vs.* current density in 5 M NaCl soln. pH 1, 40°C.
(○) activated and (●) passivated electrode

TABLE 1. R_Ω, R_{soln} AND R_{surface} ($\Omega \cdot \text{cm}^2$)

Temp. (°C)	R		R_{soln}	R	
	p	a		p	a
25	0.41	0.34	0.20	0.21	0.14
40	0.27	0.22	0.15	0.12	0.07
60	0.26	0.19	0.13	0.13	0.06
80	0.23	0.18	0.11	0.12	0.07

p : passivated electrode
a : activated electrode

The activation and passivation of the test electrode were carried out by polarizing it at −0.1 V (SCE) and 2.0 V (SCE) respectively.

Electrical Resistance. The galvanostatic transient method (current-interruptor method) was used for the measurements of the resistance and capacitance. A pulsed current was applied to the cell by means of an electrical switch. The rise time of the pulse was about 1 μs, and the potential decay from 2 to 6 μs after switching off was measured with a cathode-ray oscilloscope, the input impedance of which was 10^6 ohms. The steady-state potential before switching off was measured by means of a pen-recorder, the impedance of which was 10^6 ohms. The resistance polarization ($\eta_\Omega = \eta_{\text{soln}} + \eta_{\text{surface}}$) was determined by extrapolating the decay curves to $t=0$. An example of the plot of the resistance polarization *vs.* the current density

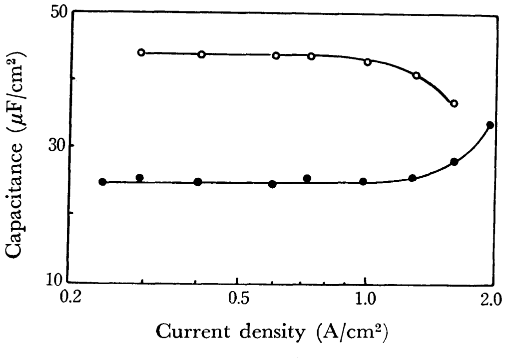
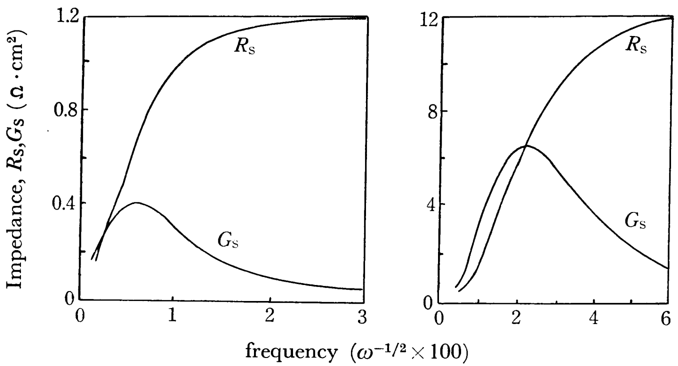


Fig. 2. Double layer capacitance of activated (○) and passivated (●) platinum electrode.
(NaCl 5M, pH 1, 25°C)

---

[1] C. C. Lu, S. Asakura, K. Fueki and T. Mukaibo, *Denkikagaku*, **38**, 213 (1970).



(a). Activated electrode (b). Passivated electrode

Fig. 3 (a), (b). Impedance of Pt electrode plotted against (frequency)$^{-1/2}$ in 5M solution, pH 1, 30°C.

is shown in Fig. 1. From the slope of the curves, the total resistance, R_Ω, was calculated.

For the determination of the R_{surface}, the test electrode was replaced by a platinized electrode of the same geometry and the R_{soln} was measured by means of an ac bridge. A preliminary experiment showed that the polarization and the resistance of the platinized platinum electrodes is negligibly small. From the values of R_Ω and R_{soln}, R_{surface} was determined. The results are summarized in Table 1.

Double-layer Capacitance. The double-layer capacitance was estimated from the decay of the electrode potential by using the equation,

$$C = -I\mathrm{d}t/\mathrm{d}E$$

where I is the current density crossing the double layer during the decay period. In order to obtain the capacitance at $t=0$, the current density before switching off was taken as the value of I, $(\mathrm{d}t/\mathrm{d}E)_{t=0}$ was determined by extrapolating the values of $\mathrm{d}t/\mathrm{d}E$ at 2, 3, 4, 5, and 6 μs to $t=0$. The results are shown in Fig. 2. As may be seen from Fig. 2, the capacitance of the passivated electrode is about half that of the activated one.

Faradaic Impedance. The faradaic impedance was determined from Lissajous's figure on a cathode-ray oscilloscope. The input voltage was sine wave. Its amplitude was 3.5 mV, and its frequency was changed from 20 Hz to 30 kHz.

In Fig. 3, the ohmic component (R_s) and the capacitive component ($G_s = 1/\omega C_s$) of the electrode impedance (Z_f) are plotted against the frequency From the shape of the curves, a surface reaction such as the recombination of chlorine atoms on the electrode is considered to be the rate-determining step.[2] The impedance of the passivated electrode was about ten times larger than that of the activated one.

---

[2] M. Breiter, Transactions of the Symposium on Electrode Process," ed. by Yeager, John Wiley & Sons, New York (1961), p. 307.