66. Remarkable Enhancement of the Rate of Cathodic Reduction of Hydrocarbonate Anions at Palladium in the Presence of Caesium Cations

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Steady-state polarization curves, representative of the electrochemical reduction of HCO_3^- ions at a smooth palladium cathode, obtained in $CsHCO_3$ and $NaHCO_3$ solutions, are compared. The net current densities, associated with the electroreduction of HCO_3^- anions, measured in 1M $CsHCO_3$ solution are shown to be up to 9 times larger than those observed in 1M $NaHCO_3$ solution. This result is interpreted in terms of a direct involvement of the Cs^+ cations in the reaction at the cathode through the formation of ion pairs with the HCO_3^- anions.

Introduction. – Recent communications, indicating that HCO_3^- ions can be reduced in aqueous solution chemically [1] and electrochemically [2] [3], using a Pd catalyst (dispersed in the solution or forming an electrode), have opened a promising way for the efficient conversion of CO_2 into easily storable compounds such as HCOOH. The electrochemical reduction of hydrocarbonate into formate

$$HCO_3^- + H_2O + 2\,e \rightarrow HCOO^- + 2\,OH^-$$

has been observed both at a supported polymercoated Pd cathode [2] and at a cathode made of smooth Pd [3]. However, in the latter case, the faradaic efficiency of long-term electrolyses was relatively low (of *ca.* 5%) [3], due to the parallel formation of palladium hydride, favoured by a partial inhibition of the hydrocarbonate reduction.

We report here new observations regarding *a*) pronounced effect of Cs^+ cations on the rate of electroreduction of HCO_3^- anions, and *b*) probable nature of the species inhibiting the above reaction.

Results and Discussion. – Since HCO_3^- ions undergo reduction within the range of potentials, close to that of the RHE, where H_2 is also formed at the Pd electrode, we considered partial currents due to the former reaction. To this end, steady-state cathodic polarization curves for the Pd electrode were also recorded in Ar-saturated borate buffer solutions having the same pH as different hydrocarbonate solutions employed. The partial current due to the hydrocarbonate reduction, corresponding to each potential, was obtained by subtracting the current measured in borate solution (assigned to the H_2 formation) from the current determined in a $NaHCO_3$ or a $CsHCO_3$ solution. While the polarization curves recorded in borate solutions were practically unaffected by the nature of the cation, the currents measured in $CsHCO_3$ solutions were substantially larger than those in $NaHCO_3$ solutions of the same concentration. Thus, the resulting partial current/potential curves for Pd in 1M $CsHCO_3$ and 1M $NaHCO_3$ show (*Figure*) a ninefold increase of the maximum rate of reduction of HCO_3^- ions on going from the $NaHCO_3$ to $CsHCO_3$ solution. The observed influence of the Cs^+ cations is most probably connected with their

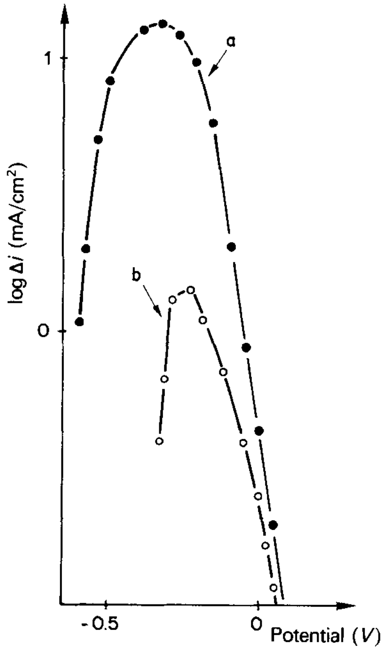

Figure. *Comparison of partial currents, assigned to the reduction of* HCO_3^- *ions at Pd, plotted* vs. *potential for* 1M $CsHCO_3$ (curve a) *and* 1M $NaHCO_3$ (curve b) *solutions.* Potentials given with respect to the reversible hydrogen electrode (RHE) in the same solution.

well-known aptitude for the formation of ion pairs in the solution and in the double layer [4]. It is worthy of note that direct evidence for the involvement of cations in the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ electron transfer reaction has recently been obtained from a surface enhanced *Raman* spectroscopic (SERS) study of gold electrodes [5]. Moreover, the Cs^+ cations have previously been shown to undergo strong adsorption on Pt [6] and can be expected to behave in the same manner towards Pd, due to evident similarities in the double-layer properties of both metals [7].

The shape of the partial current/potential curves in the *Figure* suggests possible blocking of the electrode surface by some adsorbed intermediate or product of the reaction. An indication regarding the probable nature of the poisoning species was obtained from the presence of detectable amounts of formaldehyde in the products of prolonged electrolysis of hydrocarbonate solutions. In fact, HCHO is known to adsorb on Pd [8] and has previously been shown [9] to cause the inhibition of the HCOOH decomposition on a Pd catalyst. Steady-state polarization measurements performed with hydrocarbonate solutions containing increasing additions of HCHO showed more and more pronounced decrease of partial currents associated with the reduction of HCO_3^- ions. For the addition of 0.01 mol·dm^{-3} of HCHO to 1M aq. $NaHCO_3$, the partial current due to the hydrocarbonate reduction was practically annulled, the corresponding *i-E* curve coming close to that recorded in the borate solution of the same pH. This observation bears out the hypothesis according to which HCHO would selectively affect hydrocarbonate reduction. Importantly, addition of 0.01 mol·dm^{-3} of formate to a 1M

$NaHCO_3$ solution had practically no effect upon the shape of the polarization plot and the amount of the current.

Experimental. – The electrochemical measurements were performed in a two-compartment *Pyrex* cell containing 150 cm^3 of soln. The working electrode was formed by a Pd wire (0.1 cm diameter, 0.9 cm length), a large Pt sheet was the counter-electrode and $Hg/Hg_2Cl_2/0.1$ M KCl the reference electrode. All potentials are quoted against reversible hydrogen electrode (RHE) in the same solution. Before each set of measurements (corresponding to a single polarization curve), the Pd electrode was polished to a mirror finish with alumina. Polarization curves were obtained (by means of a *Wenking 68 FR 0.5* potentiostat driven by a *Wenking SMP 69* scanning potentiometer) increasing the potential step-by-step at the rate of 30 mV/min. The solns. were prepared from reagent-grade chemicals with doubly distilled H_2O. All measurements were performed at 20°.

REFERENCES

[1] C.J. Stalder, S. Chao, D.P. Summers, M.S. Wrighton, *J. Am. Chem. Soc.* **1983**, *105*, 6318; S. Chao, C.J. Stalder, D.P. Summers, M.S. Wrighton, *ibid.* **1984**, *106*, 2723.

[2] C.J. Stalder, S. Chao, M.S. Wrighton, *J. Am. Chem. Soc.* **1984**, *106*, 3673.

[3] M. Spichiger-Ulmann, J. Augustynski, *J. Chem. Soc., Faraday Trans. I* **1985**, *81*, 713.

[4] J. Hindman, *J. Chem. Phys.* **1962**, *36*, 1000; V.G. Levich, *Dokl. Akad. Nauk SSSR* **1949**, *67*, 309; *ibid.* **1959**, *124*, 869.

[5] M. Fleischmann, P.R. Graves, J. Robinson, *J. Electroanal. Chem.* **1985**, *182*, 87.

[6] V.E. Kazarinov, O.A. Petrii, *J. Electroanal. Chem.* **1970**, *27*, App. 1.

[7] A.N. Frumkin, O.A. Petrii, *Electrochim. Acta* **1975**, *20*, 347.

[8] S.S. Kuliev, V.N. Andreev, N.V. Osetrova, V.S. Bagotskii, Yu.B. Vasil'ev, *Elektrokhimiya* **1982**, *18*, 787.

[9] L.D. Burke, F.A. Lewis, C. Kemball, *J. Catal.* **1966**, *5*, 539.