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R. Cvetkovic

University Kiril and Metodij, Skopje, Yugoslavia

Branko N. Popov

University of South Carolina - Columbia, popov@engr.sc.edu

H. A. Laitinen

University of Florida

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Electrochemical Reduction of Molybdate in the Presence of Zinc Chloride in Molten Lithium Chloride-Potassium Chloride Eutectic

R. Cvetković and B. N. Popov

Faculty of Technology and Metallurgy, University Kiril and Metodij, Skopje 91000, Yugoslavia

and H. A. Laitinen*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

ABSTRACT

Two chronopotentiometric waves were observed for the electrochemical reduction of molybdate in the presence of zinc chloride, with quarter-wave potentials of -1.5V and -1.75V vs. the Pt(II)/Pt reference electrode, respectively. It was observed that an increase in the molybdate concentration causes a decrease of the first transition time indicating a chemical reaction between ZnCl_2 (which is reduced at -1.5V) and Li_2MoO_4 in the melt forming ZnMoO_4 which is sparingly dissociated in LiCl-KCl eutectic. The equilibrium constant for the observed reaction was calculated. X-ray powder diffraction patterns of the reduction product of ZnMoO_4 have been obtained.

Laitinen and Propp (1) have shown that the electrochemical reduction product of K_2CrO_4 in LiCl-KCl eutectic containing dissolved MgCl_2 is a single compound of formula $\text{Li}_x\text{Mg}_y\text{CrO}_4$, where $x + 2y = 5$. Laitinen and Hanck (2) observed that the reduction of chromate in the presence of Zn(II) was shifted from -1.0V vs. Pt(II)/Pt reference to -0.5V . Analysis of the deposit indicated the composition to be $\text{LiZn}_2\text{CrO}_4$. Laitinen and Popov (3) also observed that when chromate is reduced in the presence of NiCl_2 at 500°C the deposit approaches the composition $\text{LiNi}_2\text{CrO}_4$.

The purpose of the present research is to characterize the insoluble electrode deposit formed when Li_2MoO_4 is reduced in the presence of ZnCl_2 in LiCl-KCl eutectic. The knowledge gained through this study will contribute to the over-all understanding of molybdate electrochemistry (4, 5) and should aid the interpretation of the mechanism of the electrochemical reduction of Li_2MoO_4 in LiCl-KCl eutectic.

Experimental

Solvent.—The eutectic mixture of potassium chloride [41 mole per cent (m/o)] and lithium chloride (59 m/o) at 450°C was used as a solvent system. The LiCl-KCl eutectic was obtained from Anderson Physics Laboratories, Incorporated, Champaign, Illinois. The method of purification has been described (1).

Apparatus.—The instrumentation and equipment used in this study have been previously described (1-5).

Electrolytic cell.—The cell used in this experiment has been previously described (6). Within this cell and under an atmosphere of dry, oxygen-free argon, the solvent was allowed to collect into the fritted compartments which were used as experimental cells. At the end of the experiment the volume of each compartment was determined by titrating its chloride content, and making calculations from the known density of the melt at 450°C .

Electrodes.—The reference electrode was a platinum foil in contact with platinum(II) solution. This reference electrode has been shown to be reproducible and nonpolarizable over a long period of time (7). The Pt indicator electrode used in this study has been pre-

viously described (1-5). The electrode had a geometric area of 0.5 cm^2 and was constructed so that the glass-metal seal was always kept above the level of the melt. The platinum gauze electrodes used to prepare samples of the film, as well as the carbon electrode which served as counterelectrode in all electrochemical investigations in the melt, were constructed as described by Propp (1).

Chemicals.—All chemicals used in this study were reagent grade. ZnMoO_4 was prepared by fusion of ZnO and MoO_3 at 700°C (8) as well as by the methods described by Schultze (9), Carriere (10), and Jander (11). The product was light rose in color and has been identified by x-ray and chemical analysis as ZnMoO_4 . Those chemicals containing water of hydration were vacuum dried at 110°C before being added to the melt. Solid chemicals were added to the melt by means of a small glass spoon. A blanket of argon was kept over the melt at all times to exclude oxygen and water vapor. The purification train used in purifying the argon has been described (1-5).

Experimental techniques.—Samples of the electrode deposit resulting from the reduction were obtained by constant current electrolysis using platinum gauze electrodes. Before their insertion in the melt solution, the gauze electrodes were cleaned in boiling, concentrated HNO_3 , rinsed with distilled water, and dried at 130°C for 20 hr. After the material had been deposited on the electrode, the electrode was allowed to cool, washed with deionized water, and dried at 120°C . The deposits were then dissolved in 5 ml of concentrated nitric acid by heating on a hot plate. The zinc content of the solution was conveniently determined by a simple EDTA titration with Eriochrome Black T as the indicator. The molybdenum content of the deposit was determined by addition of an excess of Pb^{2+} which was backtitrated with EDTA using xylenol orange as the indicator. The total molybdenum was also obtained by amperometric titration with lead, a procedure developed by Aylward (12). The lithium content was determined using flame photometry, observing the Li emission at 670.8 nm . X-ray powder diffraction patterns were obtained using an 11.47-cm camera loaded with Ilford Type G x-ray film and exposed to Ni filtered $\text{CuK}\alpha$ radiation. The Cu tube was mounted in a Norlco generator. Chloride was determined by the Volhard method.

* Electrochemical Society Active Member.

Key words: fused salts, zinc molybdate, chronopotentiometry.

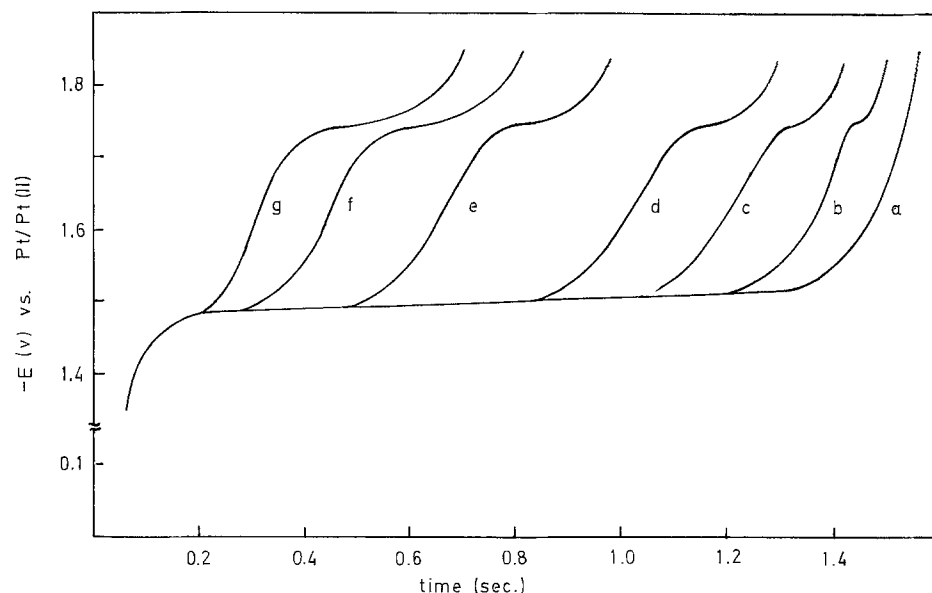


Fig. 1. Potential-time curves for chronopotentiometric reduction of mixture $\text{ZnCl}_2\text{-Li}_2\text{MoO}_4$. Current density = 50.4 mA/cm².

	Concentration of ZnCl_2 , mm	Concentration of Li_2MoO_4 , mm
a.	74	0
b.	74	7.55
c.	74	19.3
d.	74	32.7
e.	74	51.8
f.	74	87.8
g.	74	118.5

Results and Discussion

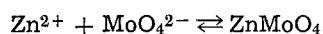
$\text{ZnCl}_2\text{-Li}_2\text{MoO}_4\text{-LiCl-KCl}$ system.—Under certain conditions one chronopotentiometric wave is observed for the reduction of Li_2MoO_4 at -1.75V vs. the Pt(II)/Pt reference electrode. This reduction was found to be diffusion controlled over the time interval investigated. Chronopotentiograms were obtained over the concentration range ($5.3 \times 10^{-3}\text{M}$ Li_2MoO_4 – $153.3 \times 10^{-3}\text{M}$). The average value of $I\tau^{1/2}/C$ calculated from the chronopotentiometric results is $175 \text{ A sec}^{1/2} \text{ mole}^{-1} \text{ cm}^3$, which agrees with the results obtained earlier (4, 5).

Chronopotentiometry of ZnCl_2 in the absence of Li_2MoO_4 revealed a wave with a quarter-wave potential of -1.5V vs. the Pt(II)/Pt reference electrode. Diffusion control was shown by the constancy of $I\tau^{1/2}/C$ at $800 \pm 4 \text{ A sec}^{1/2} \text{ mole}^{-1} \text{ cm}$ for four different concentrations ranging from $8.34 \times 10^{-3}\text{M}$ to $125 \times 10^{-3}\text{M}$ at three different current densities. The above value of $I\tau^{1/2}/C$ was used as a calibration factor for evaluating Zn(II) concentration in calculating the formation constant of ZnMoO_4 .

The effect of Zn(II) on the reduction of Li_2MoO_4 was demonstrated by successively increasing the concentration of Li_2MoO_4 at constant Zn(II) concentration as shown in Fig. 1. Two chronopotentiometric waves were observed. The first wave has a quarter-wave potential at -1.5V vs. the Pt(II)/Pt reference electrode corresponding to the reduction of Zn(II) and the other at -1.75V corresponding to the reduction of molybdate. It was observed that an increase on the molybdate concentration in the melt causes a decrease of the first transition time and at the same time an increase of the second transition time. The quantitative variation of the transition time constant was tested by running duplicates of three current densities at different Li_2MoO_4 concentrations. The decrease of $I_0\tau^{1/2}$, for the reduction step at -1.5V , with increasing Li_2MoO_4 concentration, is demonstrated in Table I.

The chronopotentiometric data for the second reduction are presented in Table II.

The data in Tables I and II can be quantitatively interpreted in terms of an equilibrium



$$K = \frac{[\text{ZnMoO}_4]}{[\text{Zn}^{2+}][\text{MoO}_4^{2-}]} = \frac{X}{(C_{\text{ZnCl}_2} - X)(C_{\text{Li}_2\text{MoO}_4} - X)}$$

The results, given in Table III indicate that $K = 30.1 \pm 2.9$, as calculated from the data in Table I.

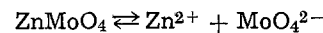
$\text{ZnMoO}_4\text{-LiCl-KCl}$ system.—In order to examine further the electrochemical reduction of Li_2MoO_4 in the

presence of ZnCl_2 , chronopotentiograms of ZnMoO_4 in molten LiCl-KCl were obtained.

Qualitatively, two chronopotentiometric waves occur in the case of ZnMoO_4 reduction with quarter-wave potentials at -1.5V and at -1.75V vs. the Pt(II)/Pt reference electrode.

The Sand equation was tested by running duplicates of four current densities at five different ZnMoO_4 concentrations. The dependence of $I_0\tau^{1/2}$ on C is demonstrated in Table IV for the first wave and in Table V for the second reduction.

The data in Tables IV and V can be quantitatively interpreted in terms of an equilibrium



In order to compare the results given in Table IV for the system ZnMoO_4 with those obtained for the system $\text{Li}_2\text{MoO}_4\text{-ZnCl}_2$ one can write for the above equilibrium

$$K = \frac{[\text{ZnMoO}_4]}{[\text{Zn}^{2+}][\text{MoO}_4^{2-}]} = \frac{(C_{\text{ZnMoO}_4} - X)}{X^2}$$

Table I. Chronopotentiometric data for the first reduction step of ZnCl_2 and Li_2MoO_4 mixtures

$$C_{\text{ZnCl}_2} = 74 \cdot 10^{-3} \text{ (M)}$$

$C_{\text{Li}_2\text{MoO}_4}$ (M)	I_0 , mA · cm ⁻²	τ , sec	$I_0\tau^{1/2}$ (A · sec ^{1/2} cm ⁻²)
$7.55 \cdot 10^{-3}$	50.4	1.20	$55.2 \cdot 10^{-3}$
	57.8	0.90	$54.9 \cdot 10^{-3}$
	69.8	0.65	$56.3 \cdot 10^{-3}$
	Avg		$55.4 \cdot 10^{-3}$
$19.30 \cdot 10^{-3}$	50.4	1.00	$50.4 \cdot 10^{-3}$
	57.8	0.70	48.4
	69.8	0.55	$51.7 \cdot 10^{-3}$
	Avg		$50.2 \cdot 10^{-3}$
$32.7 \cdot 10^{-3}$	50.4	0.75	$43.6 \cdot 10^{-3}$
	57.8	0.55	$42.8 \cdot 10^{-3}$
	69.8	0.40	$44.1 \cdot 10^{-3}$
	Avg		$43.5 \cdot 10^{-3}$
$51.8 \cdot 10^{-3}$	50.4	0.45	$33.8 \cdot 10^{-3}$
	57.8	0.40	36.6
	69.8	0.25	$34.9 \cdot 10^{-3}$
	Avg		$35.1 \cdot 10^{-3}$
$87.8 \cdot 10^{-3}$	40.4	0.40	$25.6 \cdot 10^{-3}$
	50.4	0.25	$25.2 \cdot 10^{-3}$
	57.8	0.15	$22.4 \cdot 10^{-3}$
	Avg		$24.4 \cdot 10^{-3}$
$118.5 \cdot 10^{-3}$	36.2	0.25	$18.1 \cdot 10^{-3}$
	40.4	0.20	$18.1 \cdot 10^{-3}$
	50.4	0.15	$19.5 \cdot 10^{-3}$
	Avg		$18.6 \cdot 10^{-3}$

Table II. Chronopotentiometric data for the second reduction step of ZnCl_2 and Li_2MoO_4 mixtures

$$C_{\text{ZnCl}_2} = 74 \cdot 10^{-3} \text{ (M)}$$

$C_{\text{Li}_2\text{MoO}_4}$ (M)	I_0 , mA · cm ⁻²	τ_2 , sec	$\tau^{1/2}$, sec ^{1/2}	$I_0 \tau^{1/2}$ (A · sec ^{1/2} · cm ⁻²)
7.55 · 10 ⁻³	50.4	—	—	—
19.30 · 10 ⁻³	50.4	0.05	0.025	1.26 · 10 ⁻³
	57.8	—	—	—
	69.8	—	—	—
32.7 · 10 ⁻³	50.4	0.10	0.056	2.80 · 10 ⁻³
	57.8	0.05	0.033	1.91 · 10 ⁻³
	69.8	—	—	—
			Avg	2.36 · 10 ⁻³
51.8 · 10 ⁻³	50.4	0.12	0.084	4.23 · 10 ⁻³
	57.8	0.08	0.060	3.47 · 10 ⁻³
	69.8	—	—	—
			Avg	3.85 · 10 ⁻³
87.8 · 10 ⁻³	40.4	0.30	0.204	8.24 · 10 ⁻³
	50.4	0.18	0.156	7.86 · 10 ⁻³
	57.8	0.10	0.112	6.47 · 10 ⁻³
			Avg	7.52 · 10 ⁻³
118.5 · 10 ⁻³	36.2	0.45	0.422	15.2 · 10 ⁻³
	40.4	0.35	0.294	11.9 · 10 ⁻³
	50.4	0.25	0.245	12.3 · 10 ⁻³
			Avg	13.1 · 10 ⁻³

Table III. Evaluation of equilibrium constant from Table I*

$C_{\text{Li}_2\text{MoO}_4}$ (M)	$[\text{Zn}^{2+}]$ (M)	$[\text{MoO}_4^{2-}]$ (M)	X (M)	K (M ⁻¹)
7.55 · 10 ⁻³	68.8 · 10 ⁻³	2.35 · 10 ⁻³	5.2 · 10 ⁻³	32.1
19.30 · 10 ⁻³	62.5 · 10 ⁻³	7.80 · 10 ⁻³	11.5 · 10 ⁻³	24.0
32.70 · 10 ⁻³	54.0 · 10 ⁻³	12.7 · 10 ⁻³	20.0 · 10 ⁻³	29.2
51.80 · 10 ⁻³	44.0 · 10 ⁻³	21.8 · 10 ⁻³	30.0 · 10 ⁻³	31.3
87.80 · 10 ⁻³	30.5 · 10 ⁻³	44.3 · 10 ⁻³	43.5 · 10 ⁻³	32.2
118.50 · 10 ⁻³	23.3 · 10 ⁻³	67.8 · 10 ⁻³	50.7 · 10 ⁻³	32.1
			Avg	30.2

* Standard deviation is ± 2.94 .Table IV. Chronopotentiometric data for the first reduction step of ZnMoO_4

C_{ZnMoO_4} (M)	I_0 , mA · cm ⁻²	τ , sec	$I_0 \tau^{1/2}$ (A · sec ^{1/2} · cm ⁻²)
29.05 · 10 ⁻³	14.4	1.05	14.8 · 10 ⁻³
	20.0	0.50	14.1 · 10 ⁻³
	24.4	0.38	15.1 · 10 ⁻³
	30.2	0.24	14.8 · 10 ⁻³
			Avg 14.7 · 10 ⁻³
44.3 · 10 ⁻³	14.4	1.80	19.3 · 10 ⁻³
	20.0	0.95	19.5 · 10 ⁻³
	30.2	0.46	20.4 · 10 ⁻³
	36.2	0.32	20.4 · 10 ⁻³
			Avg 20.0 · 10 ⁻³
87.9 · 10 ⁻³	30.2	1.00	30.2 · 10 ⁻³
	36.2	0.78	32.0 · 10 ⁻³
	40.4	0.60	31.3 · 10 ⁻³
	50.4	0.40	32.0 · 10 ⁻³
			Avg 31.4 · 10 ⁻³
107.0 · 10 ⁻³	30.2	1.45	36.4 · 10 ⁻³
	36.2	0.94	35.3 · 10 ⁻³
	40.4	0.74	34.7 · 10 ⁻³
	50.4	0.50	35.7 · 10 ⁻³
			Avg 35.5 · 10 ⁻³
142.7 · 10 ⁻³	30.2	1.90	41.7 · 10 ⁻³
	36.2	1.42	43.2 · 10 ⁻³
	40.4	1.10	42.4 · 10 ⁻³
	50.4	0.70	42.2 · 10 ⁻³
			Avg 42.4 · 10 ⁻³

The results given in Table VI for the equilibrium constant have been obtained using the data from Table IV.

Characterization of electrode deposit.—Samples of electrode deposit were prepared by constant current electrolysis. The cathode was immersed into 3.7 ml 0.035M ZnMoO_4 and attempts were made to prepare coulometrically the reduction product at -1.5V . It was

Table V. Chronopotentiometric data for the second reduction step of ZnMoO_4

C_{ZnMoO_4} (M)	I_0 , mA · 10 ⁻³	τ_2 , sec	$\tau^{1/2}$, sec ^{1/2}	$I_0 \tau^{1/2}$ (A · sec ^{1/2} · cm ⁻²)
29.05 · 10 ⁻³	14.4	0.50	0.216	3.76 · 10 ⁻³
	20.0	0.30	0.188	3.11 · 10 ⁻³
	24.4	0.20	0.143	3.49 · 10 ⁻³
	30.2	0.14	0.129	3.89 · 10 ⁻³
			Avg	3.56 · 10 ⁻³
44.3 · 10 ⁻³	14.4	0.85	0.290	4.18 · 10 ⁻³
	20.0	0.50	0.231	4.62 · 10 ⁻³
	30.2	0.20	0.136	4.11 · 10 ⁻³
	36.2	0.14	0.117	4.24 · 10 ⁻³
			Avg	4.29 · 10 ⁻³
87.9 · 10 ⁻³	30.2	0.55	0.245	7.24 · 10 ⁻³
	36.2	0.40	0.203	7.35 · 10 ⁻³
	40.4	0.30	0.176	7.11 · 10 ⁻³
	50.4	0.20	0.141	7.10 · 10 ⁻³
			Avg	7.24 · 10 ⁻³
107.0 · 10 ⁻³	30.2	0.80	0.295	8.91 · 10 ⁻³
	36.2	0.50	0.231	8.36 · 10 ⁻³
	40.4	0.40	0.203	8.40 · 10 ⁻³
	50.4	0.30	0.187	9.40 · 10 ⁻³
			Avg	8.77 · 10 ⁻³
142.7 · 10 ⁻³	30.2	1.05	0.338	10.21 · 10 ⁻³
	36.2	0.70	0.263	9.52 · 10 ⁻³
	40.4	0.60	0.256	10.34 · 10 ⁻³
	50.4	0.40	0.213	10.74 · 10 ⁻³
			Avg	10.20 · 10 ⁻³

Table VI. Evaluation of equilibrium constant from Table IV*

C_{ZnMoO_4} (M)	X	$(C_{\text{ZnMoO}_4} - X)$	K, M ⁻¹
29.05 · 10 ⁻³	18.38 · 10 ⁻³	10.67 · 10 ⁻³	31.6
44.30 · 10 ⁻³	24.88 · 10 ⁻³	19.42 · 10 ⁻³	31.4
87.80 · 10 ⁻³	39.20 · 10 ⁻³	48.60 · 10 ⁻³	31.7
107.0 · 10 ⁻³	44.40 · 10 ⁻³	62.60 · 10 ⁻³	31.7
142.7 · 10 ⁻³	52.90 · 10 ⁻³	89.80 · 10 ⁻³	32.1
			Avg 31.7

* Standard deviation is ± 0.23 .

possible to monitor the electrode potential only at -1.65V vs. Pt(II)/Pt reference electrode using current densities of 10, 20, 30, and 40 mA/cm². Examination of the cathode showed only one type of solid product, a dark brown solid which adhered to the surface of the electrode. Following electrolysis, the samples were washed with distilled water and dried at 130°C.

Qualitatively, the electrode deposit was found to contain Li, Zn, and Mo. Samples of the deposit were analyzed by the methods described. Table VII summarizes the composition of four samples of deposit prepared under identical conditions. If it is assumed that the deposit contains only Li, Mo, Zn, and O, one obtains the empirical formula $\text{Li}_2\text{Zn}_{0.5}\text{MoO}_4$ or $\text{Li}_4\text{ZnMo}_2\text{O}_8$. On the other hand it is not possible from the data given in Table VII to obtain the exact oxidation state of Mo, both because it was supposed that O = weight percentages add up to 100% of the sample weight and because some ZnMoO_4 may be incorporated into the deposit during the electrolysis. ZnMoO_4 is not soluble in water or any other suitable solvent. X-ray diffraction studies were therefore carried out on the dried sample.

Table VII. Typical analysis of ZnMoO_4 deposit prepared at constant current

	A	B	C	D
Sample weight, mg	32	35.3	43.5	61.4
Li, per cent weight	6.68	6.80	6.75	6.70
Zn, per cent weight	15.84	15.65	15.60	15.79
Mo, per cent weight	46.65	46.95	47.12	47.02
Per cent weight O = to 100	30.83	30.60	30.53	30.49
Empirical formula				
(A) $\text{Li}_{1.98}\text{Zn}_{0.5}\text{MoO}_{3.98}$		(B) $\text{Li}_{2.00}\text{Zn}_{0.49}\text{MoO}_{3.91}$		
(C) $\text{Li}_{1.98}\text{Zn}_{0.49}\text{MoO}_{3.89}$		(D) $\text{Li}_{1.97}\text{Zn}_{0.49}\text{MoO}_{3.89}$		

Table VIII. X-ray powder diffraction pattern of ZnMoO_4 deposit prepared at constant current

d (Å)	I/I ₀
4.770	20
4.095	20
2.9595	30
2.4815	80
2.380	10
2.0805	100
1.8924	5
1.8464	5
1.6848	20
1.5876	50
1.4904	40
1.4576	40

The "d" spacings and relative intensities of the diffraction pattern are presented in Table VIII. The "d" spacings were not comparable with any known Mo or Zn compound listed in the ASTM files.

From the preceding study of molybdate reduction in which the product $\text{Li}_5\text{Mo}_2\text{O}_8$ was identified (4), the simplest reduction mechanism for the formation of $\text{Li}_4\text{ZnMo}_2\text{O}_8$ would involve the reduction of MoO_4^{2-} to MoO_4^{3-} , which is then incorporated into a crystal lattice with Li^+ and Zn^{2+} , in the appropriate ratio. In the absence of Zn^{2+} , both MoO_4^{2-} and MoO_4^{3-} are involved in the final product.

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Kinetics of Electrogenative Hydrogenation over Platinum Black Electrocatalyst

Stanley H. Langer* and George P. Sakellaropoulos*

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

ABSTRACT

The kinetics of the electrocatalytic hydrogenation of ethylene at positive potentials has been studied over polytetrafluoroethylene-bonded, porous platinum black electrodes in perchloric acid electrolyte. Pore diffusion was generally not a significant factor except at low concentrations of reactants. Steady-state kinetic parameters and deuterium exchange results suggest that surface reaction of hydrogen with ethyl radicals is rate limiting. A mechanistic model is proposed and examined in terms of Temkin adsorption of hydrogen atoms in the low potential region ($<0.18\text{V}$). Strong Langmuir adsorption of ethylene appears to take place for all mechanisms considered. The energy production of the electrogenerative reactor is favored by high electrolyte concentration, high alkene partial pressure, elevated temperatures, and increased catalytic loading.

Few electrocatalytic reactions have been well characterized; the frequent referral to hydrogen and oxygen electrode reactions, and not many others, in the context of "electrocatalysis" is symptomatic of this situation. The electrocatalytic nature of electrogenerative hydrogenation and the availability of significant amounts of information on the process from earlier investigations (1-6) stimulated a study of the kinetics of the hydrogenation reaction at an ethylene electrode

with porous platinum black electrocatalyst. Such kinetic information should provide an additional basis for comparison with conventional catalytic hydrogenation (7-10) and with other reactions, which utilize these and similar electrodes for generation of current.

This electrogenerative process involves the operation of a hydrogen electrode against a hydrogenating olefinic electrode separated by an aqueous, acidic, barrier electrolyte phase (1-3). The external circuit between the electrodes is regulated to allow operation at varying voltages and currents generated by the reacting species. The olefinic electrode operates at positive po-

* Electrochemical Society Active Member.

Key words: ethylene, catalysis, porous electrodes, deuterium exchange.