

## Electro-organic Synthesis of *N*-Hexyl Carbamate by Carbonylation of Methanol and Hexylamine with CO over Au Supported on Carbon Anode

Roberto G. de Leon, Ichiro Yamanaka,\* and Kiyoshi Otsuka

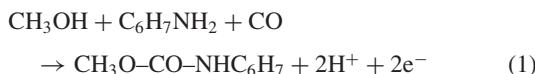
Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552

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It has been found that Au anode,  $[\text{AuBr}_3/\text{AC}+\text{VGCF}]$ , showed the electro-catalysis for carbonylation of methanol, hexylamine and CO to 6-amino-hexyl-carbamic acid methyl ester (*N*-hexyl carbamate) using LiBr electrolyte.

Amino-alkyl-carbamic acid alkylesters (*N*-alkyl carbamates) are very important chemicals and intermediates of isocyanates because of their wide application in the syntheses of intermediates, polymers, medical drugs, pesticides, et al.<sup>1</sup> Most of all *N*-alkyl carbamates have been synthesized through the phosgene route.<sup>2</sup> Some studies to avoid the drawback using phosgene have been reported in laboratory scale as candidate for green process, ex. catalytic methoxy-carbonylation of amines with dimethyl carbonate,<sup>3</sup> oxidative carbonylation of amines with CO by transition metal catalysts.<sup>2</sup> To achieve development of a new phosgene-free manufacturing process of *N*-alkyl carbamate, it is very important to propose new idea and catalyst.

Recently, we have reported the electro-carbonylation of methanol to dimethyl carbonate (DMC) with a high selectivity based on CO conversion and a high current efficiency over Pd-anode.<sup>4</sup> Thus, we propose that the electrochemical carbonylation would be a feasible method for *N*-alkyl carbamate production in this work. We have found an anode prepared from activated carbon (AC, Wako Chemical Co.) supported  $\text{AuBr}_3$  and vapor-grown-carbon-fiber (VGCF, Showa Denko Co.), and Teflon powder by the hot press-method<sup>4</sup> was active for *N*-hexyl carbamate formation at 1 atm and 298 K (eq 1).



The electrochemical carbonylation of methanol and amine was studied in a conventional H-type glass cell under potentiostatic conditions for 1 h. The anolyte components were MeOH (50 ml), hexylamine ( $3.8 \text{ mmol l}^{-1}$ ) and electrolyte ( $50 \text{ mmol l}^{-1}$ ), and the catholyte ones were MeOH and the electrolyte. A gas-mixture of CO (50.5 kPa) and Ar (50.5 kPa) was bubbled into the anolyte. Products were analyzed by GC.

We have found that Au-mesh was active for the *N*-hexyl carbamate formation after Ru, Rh, Pd, Ir, Pt, and Au meshes were tested as anodes. In addition, DMC as secondary product and trace amounts of  $\text{CO}_2$  and  $\text{O}_2$  were formed during the electrolysis. The total current efficiency was less than 100%, which proposed formation of unknown products, ex. alkyl-N-oxide, brominated compound,  $\text{Br}_2$ , etc. Pd mesh was active for the DMC formation<sup>4</sup> but not for the *N*-hexyl carbamate formation. Ru, Rh, and Ir anodes were not active for the carbonylation. In the separate experiment, it was confirmed that the Au mesh did not catalyze the *N*-hexyl carbamate formation from hexylamine and DMC at

298 K. These results clearly prove that the Au anode electro-chemically catalyze the direct carbonylation of hexylamine and methanol to *N*-hexyl carbamate. The Au mesh is unique for the *N*-hexyl carbamate formation, but a very strong corrosion of Au mesh was observed because of changing transparent and colorless electrolyte solution to dark purple one.

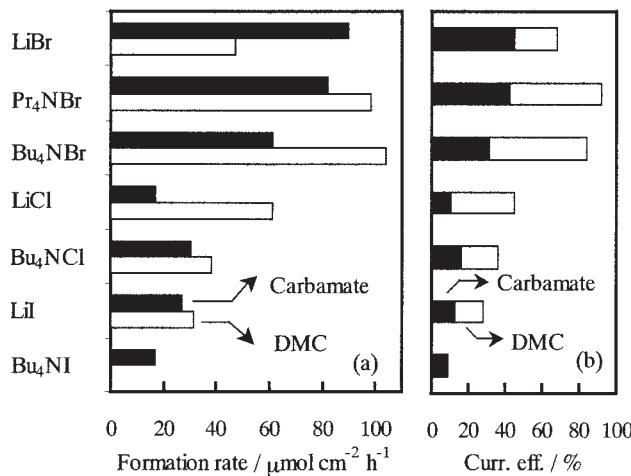
To improve stability and an electro-catalytic activity of the Au-anode, various anodes were prepared from several Au-compounds and carbon materials. We have found that an anode prepared from AC supported Au compound ( $\text{HAuCl}_4$ ,  $\text{KAuCl}_4$ ,  $\text{AuBr}_3$ ,  $\text{Au}^0$ ) and VGCF was active for the *N*-hexyl carbamate and DMC formation as well as Au mesh, as shown in Table 1. No corrosion, no change of color of electrolyte solution, was observed for the  $[\text{Au compound}/\text{AC}+\text{VGCF}]$  anodes in contrast to the Au-mesh anode. Small differences in the electro-catalytic activities for the *N*-hexyl carbamate formation were observed and the most effective anode was the  $[\text{AuBr}_3/\text{AC}+\text{VGCF}]$  because of the higher formation rate and the higher current efficiency. In addition, an  $[\text{AC}+\text{VGCF}]$  anode without Au showed no electro-catalytic activity for the carbonylation. An  $[\text{AuBr}_3/\text{AC}]$  anode without VGCF was inactive for the electrolysis due to a high electric resistance of AC. These facts clearly propose such functions of Au species as electro-catalyst, of AC as a support for Au species to prevent the corrosion, and of VGCF as a lead wire. Therefore, a strong synergism of  $\text{AuBr}_3$ , AC, and VGCF could be observed.

**Table 1.** Electrochemical carbonylation  $\text{CH}_3\text{OH}$  and *N*-hexylamine over the  $[\text{Au}/\text{AC}+\text{VGCF}]$  anode at 1.8 V (vs  $\text{Ag}|\text{AgCl}$ ) and 298 K

Anode	Id/ mA cm <sup>-2</sup>	Formation rate/ $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	
		carbamate	DMC
$\text{HAuCl}_4/\text{AC}$ +VGCF <sup>a</sup>	11.6	74.4 (34)	46.8 (22)
$\text{KAuCl}_4/\text{AC}$ +VGCF <sup>a</sup>	13.5	102 (40)	45.7 (18)
$\text{AuBr}_3/\text{AC}$ +VGCF <sup>a</sup>	12.0	97.0 (44)	44.3 (20)
$\text{Au}^0/\text{AC}$ +VGCF <sup>a</sup>	11.7	76.0 (35)	45.0 (21)
Au-mesh <sup>b</sup>	15.6	112.0 (46)	41.0 (15.5)

Anolyte: LiBr ( $50 \text{ mmol l}^{-1}$ )/hexylamine ( $3.8 \text{ mmol l}^{-1}$ )/MeOH (50 ml). P(CO) = 50.5 kPa. a) Au ( $60 \mu\text{mol}$ )/AC (50 mg)/VGCF (75 mg), b) Au ( $1729 \mu\text{mol}$ ).

Figure 1 shows the effects of various electrolytes on (a) the formation rates of *N*-hexyl carbamate and DMC and (b) the current efficiencies over the  $[\text{AuBr}_3/\text{AC}+\text{VGCF}]$  anode at 1.8 V.

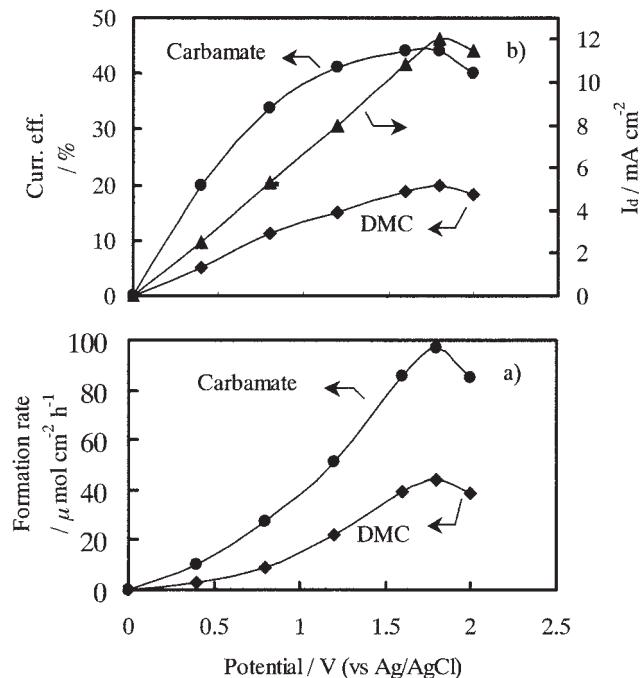


**Figure 1.** The effect of different halide-containing electrolytes on the electrochemical carbonylation of  $\text{CH}_3\text{OH}$  and hexylamine over  $[\text{Au}/\text{AC}+\text{VGCF}]$  anode,  $\text{Au}$  ( $60 \mu\text{mol}$ )/ $\text{AC}$  (50 mg)/ $\text{VGCF}$  (75 mg), at 1.8 V (vs  $\text{Ag}/\text{AgCl}$ ) and 298 K. Anolyte:  $\text{LiBr}$  ( $50 \text{ mmol l}^{-1}$ )/hexylamine ( $3.8 \text{ mmol l}^{-1}$ )/ $\text{MeOH}$  (50 ml).  $\text{P}(\text{CO}) = 50.5 \text{ kPa}$ .

First, effect of cation species of cation-Br electrolytes ( $\text{LiBr}$ ,  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$ ) on the carbonylation was studied. The order of the formation rates of *N*-hexyl carbamate was  $\text{LiBr} > \text{Pr}_4\text{NBr} > \text{Bu}_4\text{NBr}$ , in contrast, that of DMC was reverse,  $\text{Bu}_4\text{NBr} > \text{Pr}_4\text{NBr} > \text{LiBr}$ . The total current efficiency for *N*-hexyl carbamate and DMC formations of 93% using  $\text{Pr}_4\text{NBr}$  electrolyte was higher than that using  $\text{LiBr}$  (65%) and  $\text{Bu}_4\text{Br}$  (83%). Effects  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , of Li-halide electrolytes on the carbonylation are also observed in Figure 1. The formation rates of *N*-hexyl carbamate and DMC using  $\text{LiCl}$ , and  $\text{LiI}$  were considerably lower than that for  $\text{LiBr}$ . A similar effect of halide on the carbonylation was observed in  $\text{Bu}_4\text{N}$ -halide electrolytes. We could not explain how to affect cation and anion species of electrolytes on the carbonylation at the moment. We chose  $\text{LiBr}$  electrolyte for the subsequent studies because of the highest formation rate of *N*-hexyl carbamate.

Figure 2 shows (a) the formation rates of products and (b) the current efficiencies in the carbonylation as functions of anode potential over the  $[\text{AuBr}_3/\text{AC}+\text{VGCF}]$  anode at 298 K. The current and the formations of *N*-hexyl carbamate and DMC were observed over an anode potential of +0.4 V ( $\text{Ag}/\text{AgCl}$ ). The current density linearly increased with increasing anode potential but the formation rates of *N*-hexyl carbamate and DMC exponentially increased. Therefore, the current efficiencies to *N*-hexyl carbamate and DMC were increased with the anode potential. The current density and the formation rates of the products, and the current efficiencies showed the maxima at 1.8 V. This result suggested drastic changing of electro-catalysis and a state of the  $[\text{AuBr}_3/\text{AC}+\text{VGCF}]$  anode over 1.8 V.

To obtain some information of Au-species on the anode, powder XRD spectrum of the fresh  $\text{AuBr}_3/\text{AC}$  was measured and strong gold metal diffraction patterns were observed. This fact strongly suggested reduction of  $\text{AuBr}_3$  to  $\text{Au}^0$  with AC during the impregnation treatment. The average particle size of  $\text{Au}^0$  crystal



**Figure 2.** The carbonylation of  $\text{CH}_3\text{OH}$  and hexylamine over the  $[\text{Au}/\text{AC}+\text{VGCF}]$  anode as function of applied potential.  $T = 298 \text{ K}$ , anode:  $\text{Au}$  ( $60 \mu\text{mol}$ )/ $\text{AC}$  (50 mg)/ $\text{VGCF}$  (75 mg). Anolyte:  $\text{LiBr}$  ( $50 \text{ mmol l}^{-1}$ )/hexylamine ( $3.8 \text{ mmol l}^{-1}$ )/ $\text{MeOH}$  (50 ml).  $\text{P}(\text{CO}) = 50.5 \text{ kPa}$ .

was evaluated 30 nm. Therefore, a nearly real state of the fresh  $[\text{AuBr}_3/\text{AC}+\text{VGCF}]$  should be  $[\text{Au}^0/\text{AC}+\text{VGCF}]$ . We have not obtained a significant cyclic voltammogram of the anode, yet. However, from the standard redox potentials of  $\text{Au}^{3+}/\text{Au}^0 = 1.50 \text{ V}$  (NHE) and  $\text{Br}^-/\text{Br}_2 = 1.07 \text{ V}$ , the drastic changing of the electro-catalysis of the anode at 1.8 V ( $\text{Ag}/\text{AgCl}$ ) observed in Figure 3 should be related to the oxidation of  $\text{Au}^0$  to  $\text{Au}^{3+}$ . Therefore, the formation of *N*-hexyl carbamate and DMC should be catalyzed over  $\text{Au}^0$  on AC.

As described so far, we have found the electro-catalysis of the Au-anode for the *N*-hexyl carbamate formation, under suitable conditions; 20% yield (hexylamine) in 1 h, 78% selectivity (CO), 50% current efficiency. We must improve the yield and the current efficiency as well as clarify the reaction mechanism and the catalysis of the Au-anode.

## References

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