Electrochemical Reduction of CO_2 in Micropores

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CO_2 electroreduction was examined on high area nickel electrocatalysts supported on activated carbon fibers, which contain slit-shaped pores with widths on the order of nanometers. The current efficiency for CO_2 reduction to CO reached values of 70%. In contrast, much smaller amounts of CO were generated for the same type of high area nickel catalyst supported on non-activated carbon fibers. The enhancement of the CO_2 reduction selectivity with the microporous support is thought to include a nanospace effect, which gives rise to high pressure-like effects at ambient pressure.

The use of high area metallic catalysts supported on microporous media is of great interest for various reasons, including the ability to maintain metallic catalysts in a high state of dispersion. Such materials, for example, activated carbons and zeolites, are highly porous with large surface areas.[1] One of the most interesting aspects of these supports is that, with pore widths on the order of nanometers, the adsorbability of gaseous reactants can be much enhanced, and those reactants are both concentrated and contained in small spaces. Thus, microporous materials provide a medium in which unusual effects can occur, which have been termed nanospace effects.[2,3] Nanospace effects include the ability to mimic a high-pressure environment: because of the support's enhanced capacity for adsorption, the products of certain types of reactions may be similar to those found at high pressures with conventional catalyst supports.[4] This effect can be quite attractive in cases in which desirable products are favored by high-pressure conditions, e.g., CO_2 reduction.

In the present work, CO_2 electrochemical reduction was examined on high area metal electrocatalysts supported on activated carbon fibers (ACF), which contain slit-shaped pores with widths on the order of nanometers. Such electrocatalysts were used in the form of fuel cell-type gas diffusion electrodes (GDEs). GDEs can be operated at high current densities, due to enhanced mass transport of gases through very thin liquid films in the three-dimensional structure. When a dispersed metal catalyst supported on ACF is within the so-called three-phase (gas-liquid-solid) boundary region, it can be efficiently provided with electrons, CO_2, and charge-balancing ions, e.g., protons.

The ACF-supported metal catalysts were prepared as follows. The fibers were placed in contact with aqueous solutions of the metal nitrates and were stirred at room temperature (~10 h). The fibers were then washed with water, and the adsorbed metal ions were reduced under hydrogen atmosphere at 350 °C after drying. For the GDE active layers, a mixture of carbon black, for example, acetylene black (AB) (Gunbai, Denki Kagaku Kogyo) and PTFE (Daikin D-1) was ultrasonically dispersed in water. The gas diffusion layer contained AB and PTFE in a 3:1 weight ratio, whereas the active layer contained AB, PTFE and ACF in a 9:3:1 weight ratio. The mixture of carbon black and PTFE was dried using a rotary evaporator and was then pressed, together with a stainless mesh, using a die to form a disk-type electrode, 13 mm in diameter. The apparent surface area of the working electrode was 0.49 cm^2. This electrode was then heat-treated at 350 °C in a hydrogen atmosphere. A three-compartment electrochemical cell was used. CO_2 was fed into the gas compartment and 0.5 mol L^{-1} $KHCO_3$ aqueous solution was used as the electrolyte. Oxygen was removed by sparging with argon before the electrolysis. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and counter electrode, respectively. The electrolysis was carried out using a potentiostat-galvanostat (Hokuto HA-501) with a coulometer (Hokuto HF-201). The electrode potential was corrected using an I-R compensator (Hokuto HI-203). The reduction products were analyzed using a gas chromatograph (Ohkura GC-202, Porapak-Q column, FID; Hitachi 163, MS-13X column, TCD), and a high performance liquid chromatograph (Tosoh UV-8010, Shodex KC811 column, 210 nm UV).

To investigate the effect of micropores, we conducted electrolyses using the following catalysts, unmodified ACF

Table 1. Reduction products for various catalysts at -1.8V vs. SCE

Catalyst	Specific Surface Area[a]	Current Efficiency / %					Current Density/ mA cm^{-2}	
		H_2	CO	CH_4	HCOOH	Total	Total	CO_2 tot.[b]
ACF only	1500	84.69	2.30	0.22	0.00	87.21	125	2.88
CF/Fe	----	69.40	0.11	0.05	0.00	69.56	94	0.15
ACF/Fe	----	64.10	0.16	0.28	9.05	73.58	78	7.40
CF/Ni	----	80.48	3.38	0.08	0.00	83.94	109	3.68
ACF/Ni-1	700	69.88	2.86	0.15	12.17	85.06	31	4.77
ACF/Ni-2	1300	53.14	30.31	0.14	0.00	83.66	47	14.25
CF/Pd	----	89.97	0.47	0.21	0.00	90.70	60	0.41
ACF/Pd	----	81.37	6.17	0.80	0.00	88.30	50	3.47

[a] BET surface area, m^2 g^{-1} [b] CO_2 reduction partial current density, mA cm^{-2}

(ACF only), iron, nickel, and palladium catalysts supported on non-activated carbon fibers (CF/Fe, CF/Ni, CF/Pd), iron and palladium catalyst supported on activated carbon fibers (ACF/Fe, ACF/Pd), and two types of nickel catalysts supported on activated carbon fibers (ACF/Ni-1, ACF/Ni-2). Table 1 shows the reduction product distributions for the various catalysts at -1.8 V vs. SCE. The ACF support itself has very little activity for CO_2 reduction, and hydrogen evolution was the principal reaction. The CF/Fe, CF/Ni and CF/Pd catalysts showed little activity as well. The ACF/Fe and ACF/Ni catalysts, however, showed significant activity for CO_2 reduction. These results can be understood in the light of the work of Hara, et al., on electrochemical reduction with high pressure CO_2.[5-8] These workers found that, at high CO_2 pressures, the adsorption equilibrium on Ni, for example, was shifted in favor of CO_2, which displaced strongly bound CO. Iron and nickel bulk electrodes show little activity for CO_2 reduction at ambient pressure.[9,10] However, with high pressure CO_2, these metals showed high activity for CO_2 reduction. In this case, we achieved electroreduction under high pressure-like conditions assisted by the nanospace effect. The differences in behavior for the Fe, Ni and Pd catalysts supported on ACF will be examined in a separate publication.[11]

We have also examined in more detail the influence of the support. For example, the main difference between two samples, ACF/Ni-1 and ACF/Ni-2, which were prepared slightly differently (the first being prepared using a vacuum pore-filling technique), was the specific surface area. The ACF/Ni-1 catalyst showed a greatly reduced surface area compared to unmodified ACF, whereas the ACF/Ni-2 catalyst showed a smaller reduction. The ACF/Ni-2 catalyst also showed higher CO_2 reduction activity than the ACF/Ni-1 catalyst. The difference in the product distributions is due simply to the fact that the micropores were blocked, and thus the nanospace effects were no longer operative. This result clearly demonstrates that the microporous support is playing a role in the CO_2 reduction electrocatalysis (Figure 1).

Finally we measured the reduction product distribution at various potentials for the ACF/Ni-2 catalyst, (Figure 2). The highest current efficiency for CO_2 reduction to CO reached a value of approximately 70% at -1.6 V (partial current density of ~7 mA cm^{-2}). In contrast, negligible amounts of CO are typically generated on conventional nickel catalysts at ambient pressure. The CO_2 reduction partial current density increased monotonically with increasingly negative potential and then reached a plateau of ~20 mA cm^{-2} at ~-2.0V, probably due to CO_2 mass transport within the pores.

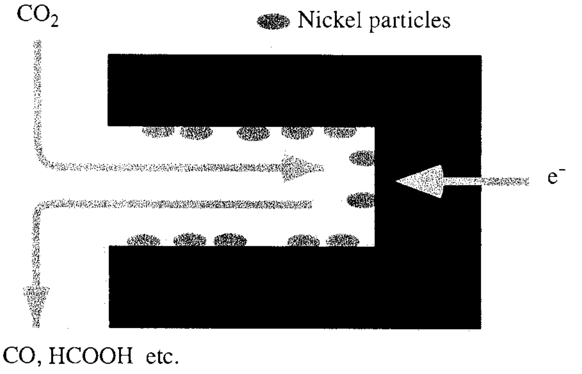

Figure 1. Schematic diagram of CO_2 reduction in a slit-shaped pore of nanometer dimensions with dispersed Ni nanoparticles.

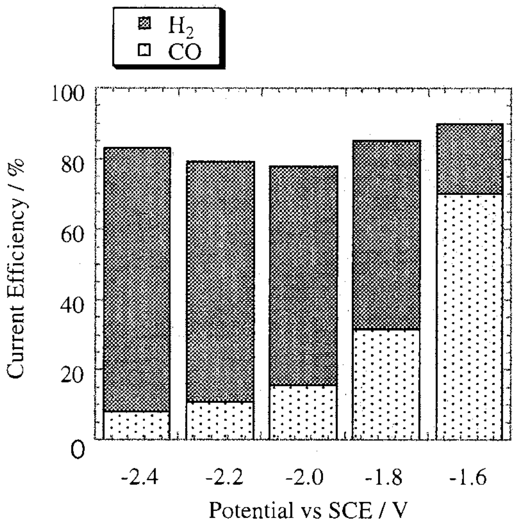

Figure 2. Dependence of current efficiencies for CO and H_2 production on potential for Ni/ACF electrocatalysts.

Work is now in progress to improve the CO_2 reduction performance of ACF-supported transition metal catalysts still further. In addition, the characterization of such electrocatalysts is also under way.

References and Notes

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