

# GLOBAL WARMING

## Electrochemists Enlisted in War

### The Carbon Dioxide Reduction Battle

by Donald A. Tryk and Akira Fujishima

**D**uring the past two years or so, the topic of global warming has been heating up. It seems that not a day goes by when there is nothing in the newspaper or on the evening news about it. If there is an unseasonably hot day or unusual weather pattern, we often blame it on global warming. Most people agree that the Earth is slowly warming up; many climate scientists project increases of 2 to 5°C by the end of the 21<sup>st</sup> century.<sup>1</sup> Natural questions inevitably arise: Are we causing this warming? Is it dangerous? Is there anything we electrochemists can do about it? Answering even the first of these questions is incredibly complex; large teams have been devoting themselves over periods of many years to the measurement of temperatures and greenhouse gas concentrations. Some of these measurements, involving H:D and <sup>16</sup>O:<sup>18</sup>O ratios in polar ice cores, have been able to extend the time scale back as far as 160,000 years.<sup>2</sup> These results show that we now enjoy a global temperature that is approximately 6°C warmer than that during the depths of the recent ice ages, and we only need an additional 2°C to equal the hottest temperature, which occurred 120,000 years ago. We will probably reach that point within the next 100 years.

Is this due to CO<sub>2</sub> generated by human activity? There is little doubt that we are generating huge amounts of CO<sub>2</sub>. The numbers stagger the imagination: during 1990, we generated about 6.2 Gt of carbon in the form of CO<sub>2</sub> as a result of the burning of fossil fuels, and the equivalent of 1.3 Gt as a result of deforestation, for a total of 7.5 Gt (1 Gt C = 3.7 Gt CO<sub>2</sub>; 1 gigaton = 10<sup>9</sup> metric tons or 10<sup>15</sup> grams).<sup>3</sup> For comparison, the total present amount of carbon in the atmosphere is estimated to be 720 Gt.<sup>4</sup> A simple extrapolation of the 1990 rate leads to a doubling of the amount of CO<sub>2</sub> in the atmosphere by the year 2100. The greenhouse effect due to CO<sub>2</sub> is inarguable: it leads to a gain of approximately 30-40°C in aver-

age global temperature compared to that expected simply on the basis of the Earth's distance from the Sun, corrected for reflection losses.<sup>5</sup> This can be contrasted with the greenhouse effect on Venus, whose atmosphere consists mostly of CO<sub>2</sub> and whose average temperature exceeds 400°C, almost 500°C greater than the reflection loss-corrected expected value. The physics of the greenhouse effect are simple: the Sun warms the Earth, which can be thought of as a 255K black-body. The peak in the Earth's black-body radiation occurs at 15 μm, which just happens to coincide with an intense absorption peak for CO<sub>2</sub>.<sup>6</sup>

Is this warming effect dangerous? Here we get into an area that is even more hotly debated than those already mentioned. However, if one polled the people around the globe who are most likely to be affected in the near future by the warming trend (for example, those living on small islands or river deltas or even those living in areas that have recently been subjected to severe flooding), one may find that they are a bit more impatient with the debate than the rest of us.<sup>1</sup> This article is intended to familiarize readers with the current literature, both scientific and popular.

Now for the more immediate questions. What can we do about it, both as ordinary citizens and as electrochemists,

and finally, what are electrochemists doing now? As ordinary citizens, we need to educate ourselves as thoroughly as possible on this issue, keeping in mind that there are conflicting views being expressed. Increasingly, we may have the feeling that something should be done as soon as possible, at least in terms of research, even before all of the previous questions have been answered. In general, physical scientists can make major contributions by devising ways to conserve energy and to generate renewable energy. More particularly, chemists have been working on various ways to deal with CO<sub>2</sub>, including removal, sequestration, utilization, and conversion into fuels.<sup>7</sup> There has been significant work aimed at mimicking natural photosynthesis in extremely inventive fashion.

There has been a long-standing effort to use electrochemical approaches to directly convert CO<sub>2</sub> into various types of fuels.<sup>7</sup> However, there is not a general consensus that this is a useful endeavor. When we talked recently to two well-known electrochemists, we were met with skepticism. Both pointed out that one must first burn a fossil fuel, generating CO<sub>2</sub>, to generate the electrical energy with which to reduce CO<sub>2</sub>, so that the whole exercise is worse than doing nothing at all. In fact, the only way in which such an approach makes sense is one in

Table I. Selected free energies and standard potentials for CO<sub>2</sub> reduction reactions.

Reaction	ΔG <sup>0</sup> , kJ mol <sup>-1</sup>	E <sup>0</sup> , V vs. SHE
CO <sub>2</sub> (g) + 2H <sup>+</sup> + 2e <sup>-</sup> ↔ CO(g) + H <sub>2</sub> O	+20.06	-0.104
CO <sub>2</sub> (g) + 8H <sup>+</sup> + 8e <sup>-</sup> ↔ CH <sub>4</sub> (g) + 2H <sub>2</sub> O	-130.62	+0.169
CO <sub>2</sub> (g) + 6H <sup>+</sup> + 6e <sup>-</sup> ↔ CH <sub>3</sub> OH(aq) + H <sub>2</sub> O	-17.24	+0.030
CO <sub>2</sub> (solv.) + e <sup>-</sup> ↔ •CO <sub>2</sub> <sup>-</sup> (solv.)	+183.32	-1.900
2CO <sub>2</sub> (g) + 2e <sup>-</sup> ↔ CO(g) + CO <sub>3</sub> <sup>2-</sup>	+123.74	-0.641

These values (for pH 0 for reactions involving protons) were calculated on the basis of thermodynamic data given in the *Atlas of Electrochemical Equilibria in Aqueous Solutions*, by M. Pourbaix, Section 17.1, Pergamon Press, Oxford (1966); *Physical Chemistry*, Sixth Edition, by P. W. Atkins, Oxford University Press, Oxford (1998); and *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, by F. R. Keene, B. P. Sullivan, K. Krist, H. E. Guard, Editors, Chapter 1, Elsevier, Amsterdam (1993).

which non-fossil energy is used. For example, after installation at least, solar, wind, geothermal, and nuclear energy do not contribute significantly to CO<sub>2</sub> generation.

With the photoelectrochemical approach, the solar energy harvesting process is incorporated into the same system. If this can be done without sacrificing any of the performance characteristics of separate electrochemical and light-harvesting systems, there could be benefits in terms of cost and space saving.

What are the advantages of electrochemical vs. chemical reduction? One is that water can be used as the source of hydrogen.<sup>7</sup> Thus, instead of first electrolytically generating hydrogen, one can directly hydrogenate CO<sub>2</sub>. Another advantage, which is a general one for electrochemical processes, is that reactions can be carried out at room temperature, because the driving force is potential rather than elevated temperature.

### Reactions, Thermodynamics, and Kinetics

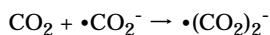
**Basic reactions.**—The solubility and acid-base equilibria involving CO<sub>2</sub> have been well-known to most of us since our student days. The carbonic acid-bicarbonate buffer system is responsible for keeping our blood at the proper pH (7.35-7.45). The hydration and dehydration reactions are slow, so that our bodies require the enzyme carbonic anhydrase to catalyze these reactions, whereas all of the others are considered to be quite fast.

Several representative reduction reactions are listed in Table I, together with the corresponding standard redox potentials. Most of the reductions of CO<sub>2</sub> occur in a potential range of about 400 mV, centered near the reversible potential for hydrogen evolution (RHE). Thus, the theoretical cell voltages for electrolytic cells that produce the listed compounds via CO<sub>2</sub> reduction at the negative electrode

and oxygen evolution at the positive electrode, are rather close to that for a water electrolysis cell.

However, the one-electron reduction to the radical anion •CO<sub>2</sub><sup>-</sup> occurs at a much more negative potential. If •CO<sub>2</sub><sup>-</sup> is an intermediate in CO<sub>2</sub> reduction, one might expect large negative potentials to be required. However, this species is quite reactive, and thus, even if it is involved, its concentration could be quite low, and CO<sub>2</sub> reduction could then take place at much less negative potentials. For example, even in non-aqueous solution, it is possible to reduce CO<sub>2</sub> at more positive potentials, as in the reduction to produce CO and carbonate (last reaction in Table 1).

Another interesting possibility is that •CO<sub>2</sub><sup>-</sup> can be greatly stabilized if it forms a complex with neutral CO<sub>2</sub>.



This species is stable even in the gas phase and has a positive electron affinity (+0.9 eV), compared to a negative value for •CO<sub>2</sub><sup>-</sup> itself (-0.6 eV). This adds up to an expectation that the dimer radical could be as much as 1.5 V easier to produce electrochemically than the simple radical. This can be important also when we consider electrocatalysis in a moment.

**Kinetics, mechanisms, and catalysis.**—There are a number of research groups that have been dedicating their efforts to fundamental studies of the kinetics of CO<sub>2</sub> reduction on a variety of electrode surfaces, including most of the metals in the periodic table, a number of alloys, metal oxides, semiconductors, and transition metal complexes, including phthalocyanines and porphyrins. One of the best studied metals has been copper. The interest in copper stems from its ability to produce hydrocarbons and alcohols in relatively high yields. On other surfaces,

there is a higher selectivity for the production of CO or formate. One of the most active groups over the years in this area has been that of Professor Yoshio Hori of Chiba University.

In aqueous solution, there is an almost unavoidable competition between CO<sub>2</sub> reduction and H<sub>2</sub> evolution (HE) because of the ubiquity of water molecules and the fact that the standard potentials are quite close to each other. There are several ways of minimizing this problem, including choosing electrode materials with very high overpotentials for HE, such as Sn, In, Bi, Sb, Cd, Zn, Pb, Ga and C; choosing materials with higher affinities for CO<sub>2</sub>; and operating under high CO<sub>2</sub> pressures to increase the coverage of adsorbed CO<sub>2</sub>. Regarding the first approach, we have recently been investigating the use of conductive diamond electrodes because of the extremely high overpotentials for HE.

The reaction pathways and resulting product distributions can be quite complex, because they are related to the energies of adsorption of a whole range of possible species, including reactants, intermediates and products. Of course, it is highly desirable to obtain quantitative conversion to a single product to avoid the need for separation. For example, if CO<sub>2</sub> researchers could produce a hydrocarbon such as methane or an alcohol such as methanol directly at close to 100% current efficiency, they would consider the battle at least partly won. Thus far, this has been achieved only for carbon monoxide and formate.

Getting back to the example of the CO<sub>2</sub> dimer radical anion, it has been found by researchers in Germany that this species can adsorb very nicely on Ni(110) single crystal surfaces (Fig. 1a). Here we show what it would look like if the theoretically calculated configuration (Fig. 1b) is simply parked on the surface of the single crystal. This picture indicates

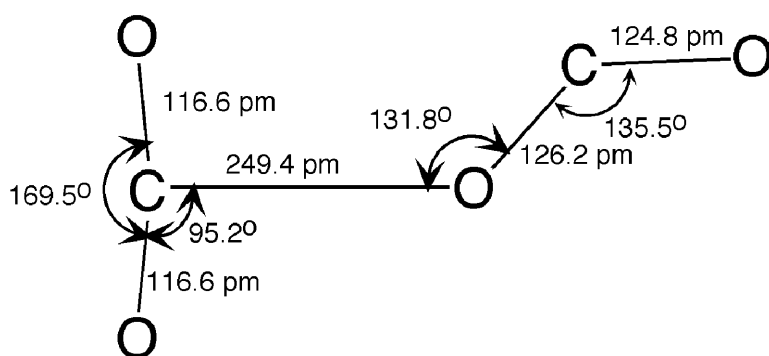
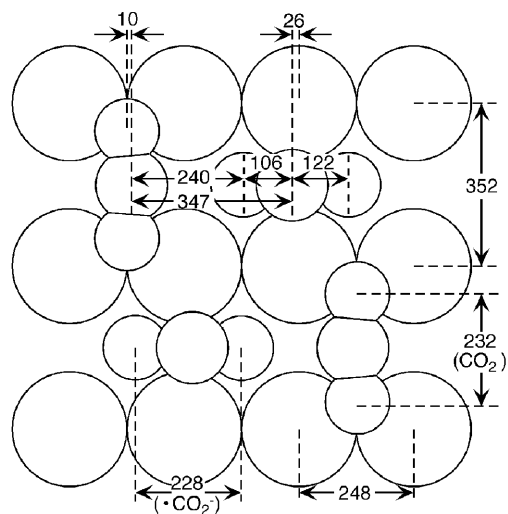


FIG. 1a. (left photo) Schematic diagram for the adsorption of •(CO<sub>2</sub>)<sub>2</sub><sup>-</sup> on Ni(110), based on Fig. 9 in H.-J. Freund and R. P. Messmer, *Surf. Sci.*, 172, 1 (1986). The registry has been shifted 128 picometers along the "rails," to improve the fit to the surface atoms.

FIG. 1b. (top photo) Diagram of the theoretical bond distances and angles for •(CO<sub>2</sub>)<sub>2</sub><sup>-</sup> based on Fig. 1 of H. R. Rossi and K. D. Jordan, *J. Chem. Phys.*, 70, 4422 (1979).

**Table II. Representative results for electrochemical CO<sub>2</sub> reduction at solid electrodes and gas-diffusion electrodes.**

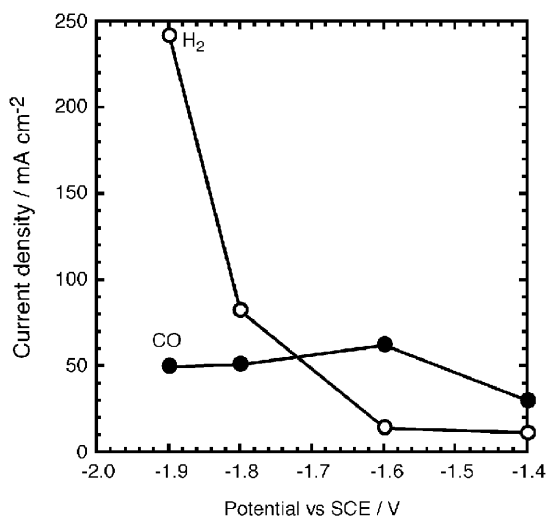
Electrode	Electrolyte	T, K	P, atm	CE, %	Product	PCD, mA cm <sup>-2</sup>	Potential V	Reference Electrode	Author	Year
<b>Solid Electrodes</b>										
Cu	TBABF <sub>4</sub> /CH <sub>3</sub> OH	298	40	87	CO	288	-2.3	Ag	Saeki	1995
In	KHCO <sub>3</sub> /H <sub>2</sub> O	298	60	108	HCOOH	215			Todoroki	1995
Ag	KOH/CH <sub>3</sub> OH	248	1	90	CO	18	-6.0	SCE	Kaneco	1998
BDD	TBABF <sub>4</sub> /CH <sub>3</sub> OH	298	40	42	CO	84	-4.0	W	Aoyagi	2000
<b>GDE</b>										
Cu	KOH	298	1	69	C <sub>2</sub> H <sub>4</sub>	268	-3.0	Ag/AgCl	Cook	1990
Pt	KHCO <sub>3</sub>	298	30	35	CO	313	-1.22	Ag/AgCl	Hara	1995
Ag	KHCO <sub>3</sub>	298	20	86	CO	258	-1.92	Ag/AgCl	Hara	1997
Ag	KOH	298				3050			Hara	1997
Pt	KHCO <sub>3</sub>	298	20	39	CH <sub>4</sub>	233	-1.93	Ag/AgCl	Hara	1997
CoTPP	KHCO <sub>3</sub>	298	20	97	CO	97	-0.96	Ag/AgCl	Sonoyama	1999
Ni/ACF	KHCO <sub>3</sub>	298	1	67	CO	60	-1.6	SCE	Yamamoto	2000

Abbreviations: BDD (boron-doped diamond), CE (current efficiency), CoTPP (cobalt tetraphenylporphyrin), GDE (gas-diffusion electrodes), PCD (partial current density), TBABF<sub>4</sub> (tetrabutylammonium tetrafluoroborate). In some cases, the reported potentials have been corrected for ohmic resistance.

that the bonds have to be stretched a small amount to line up perfectly with the Ni atoms. This could result in the activation of the complex so that it decomposes more easily to CO and carbonate. The tendency of this dimer species to be stabilized on various surfaces probably depends upon electronic as well as geometric factors. For example, although the sizes of copper atoms are very similar to those of Ni, the dimer is not known to exist on copper (110) surfaces. In other cases, *e.g.*, Ag metal, on which high current efficiencies for CO production are observed, it is also possible that the •(CO<sub>2</sub>)<sub>2</sub> species is stabilized.

The next step, remembering the potential urgency of our efforts, is to consider how to maximize the efficiency for the generation of a particular product, for example, a fuel. Either we must decrease the potential at a given current (specifically, the partial current density for a particular product) or increase the current at a given voltage.

**Avoiding mass transport limitations: high pressure and gas-diffusion electrodes.**—In many cases, we are limited at least partially by the solubility of CO<sub>2</sub>. There are two main ways to get around this problem, to use high pressure or to use gas-diffusion electrodes. A third approach is to do both. A fourth approach, used by Professor Satoshi Kaneco of Mie University in Japan, is to use low-temperature methanol, which is an industrially used CO<sub>2</sub>-absorber.<sup>8</sup> A number of researchers have been intensively pursuing these approaches. The results show that it is possible to increase the current



*Fig. 2. Partial current densities for CO and H<sub>2</sub> production in CO<sub>2</sub>-saturated (1 atm) 0.5 M KHCO<sub>3</sub> at a gas-diffusion electrode prepared from Ni-catalyzed activated carbon fibers.*

densities greatly (Table II), with some workers achieving quite large values, particularly in the case of elevated CO<sub>2</sub> pressure.

Our group has recently extended our previous work with high-pressure CO<sub>2</sub> in methanol (see entry for Saeki in Table II), in which the solubility of CO<sub>2</sub> is extremely high (approximately 7.5 M at 40 atm). On heavily boron-doped diamond electrodes, we have obtained high current efficiencies (42%) and high partial current densities (84 mA cm<sup>-2</sup>) for CO production, with the balance being almost entirely hydrogen. We have recently obtained even better results with silver electrodes. It is important to note that the counter electrode is immersed in an aqueous solution, so that it can evolve oxygen gas instead of oxidizing methanol. The latter process would obviously not be useful.

The gas-diffusion electrode approach is an extremely promising one, with some of the best results coming from the group of Professor Tadayoshi Sakata at Tokyo Institute of Technology. They have obtained the very interesting result that an inverted Pt-GDE (catalyst side facing gas) is more effective than the same electrode in the normal configuration.<sup>9</sup>

In our laboratory, we have also been pursuing the gas-diffusion electrode approach, but with a modification. Work of Professor Katsumi Kaneko and coworkers at Chiba University has indicated that there are unusual adsorption effects in slit-shaped micropores in activated carbon fibers, such that very high effective gas pressures can exist.<sup>10</sup> These high pressures can greatly enhance the formation of products of certain types of reactions. Taken together with results of Professor Sakata's group, who had shown

that high pressure CO<sub>2</sub> can significantly enhance CO<sub>2</sub> reduction on smooth Ni, these results indicate that it should be possible to enhance CO<sub>2</sub> reduction of fine particles of Ni dispersed on the walls of activated carbon fibers. Indeed this has turned out to be the case. We have found that it is possible to achieve current efficiencies for CO production as high as 67%, with a partial current density of ca. 50 mA cm<sup>-2</sup> (Fig. 2).<sup>11</sup> The major products are H<sub>2</sub> and CO, and, by varying the potential, we are able to control the ratio of these two gases,



Fig. 3. Rectangular cell for CO<sub>2</sub> reduction with 2 x 2 cm gas-diffusion cathode.

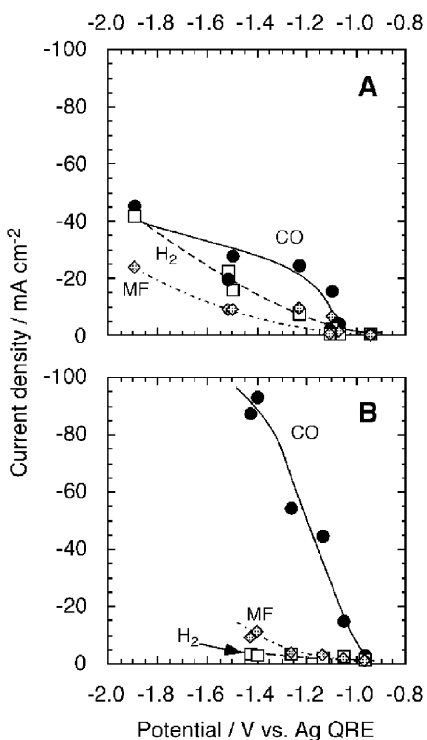
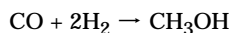


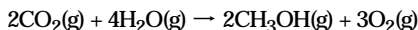
Fig. 4. Partial current densities for the photoelectrochemical production of CO and H<sub>2</sub> in CH<sub>3</sub>OH at (a) 1 atm CO<sub>2</sub> and (b) 40 atm CO<sub>2</sub>. MF stands for methyl formate, which is the reaction product of formate and methanol.

meaning that it is possible to directly produce synthesis gas with various compositions. For example, with a 2:1 ratio, it would be feasible to synthesize methanol



This reaction is exothermic and can be carried out catalytically with catalysts developed by various groups, including that of Professor Kaoru Fujimoto of the University of Tokyo. Methanol could be used in fuel cells for electric power generation. We should also note that dimethyl ether is another fuel that can be produced from syngas. It is now being considered as a clean-burning replacement for diesel fuel in vans and buses.

Our experiments have been carried out with a small electrode (effective area 0.5 cm<sup>2</sup>) in an H-type cell, but we have recently scaled up to a 2 x 2 cm electrode mounted in a rectangular cell with a relatively small inter-electrode gap (1-2 mm) in order to minimize ohmic losses (Fig. 3). Preliminary results show that it is possible to achieve an approximately 1:1 (v/v) gas ratio at a current density of 10 mA cm<sup>-2</sup> and a cell voltage of 3.05 V, producing O<sub>2</sub> at the counter electrode. Based on an enthalpic voltage of 1.36 V, this constitutes an overall efficiency of 44.6%. Obviously, this needs to be improved. We can also produce a 2:1 ratio at a slightly higher voltage (3.60 V). If we speculate for the moment that we could convert the CO and H<sub>2</sub> to methanol catalytically without any additional energy input, the overall reaction could be written as follows



The enthalpic potential for this reaction is 1.169 V, for which the calculated efficiency would be 32.5%, which is reasonable, considering the fact that we will have wasted some energy in producing methanol.

Of course, it is necessary to compare the electrochemical method for producing syngas with conventional ones such as steam reforming, partial oxidation of methane and CO<sub>2</sub> reforming of methane. Two of these processes are quite endothermic (SR and CRM), but the electrochemical route is even more endothermic, for two reasons, it does not use methane as a reactant, and it explicitly includes the energy cost of producing hydrogen. Given the demonstrated effectiveness of electrochemical reduction of CO<sub>2</sub> to either pure CO or CO plus H<sub>2</sub> (Table II), it is our opinion that it is high time to start considering the development of fuel cells based on this technology. It is also necessary to

start considering the integration of such cells into complete systems, including CO<sub>2</sub> supply, energy supply, and delivery of pure product.

## Photoelectrochemistry

As we have already mentioned, the photoelectrochemical (PEC) approach involves the energy harvesting process intrinsically, in a kind of artificial photosynthesis.<sup>7,12</sup> This idea is very appealing, and various groups have taken up this worthy challenge over the past 20 years, ever since Professor Martin Halmann of the Weizmann Institute studied CO<sub>2</sub> reduction on illuminated GaP. The group of Professor John Bockris (formerly at Texas A&M) was active in this area, as well as that of Professor Yoshihiro Nakato of Osaka University currently. The latter has achieved rather promising results with Cu and Au-decorated Si photoelectrodes in aqueous solution.<sup>13</sup>

In our laboratory, we have extended the high-pressure CO<sub>2</sub>/methanol system further, with the PEC approach, using p-InP, p-GaP and p-Si.<sup>14</sup> With all of these electrodes, we can obtain very high current densities and current efficiencies, approaching 100% for CO production. The best results have been with p-InP, at which we have obtained 92% CE at a PCD of 95 mA cm<sup>-2</sup> for CO (Fig. 4). The onset potential was approximately -0.8 V vs. a silver QRE, which we have converted to -0.5 V vs. SHE. This is 1.4 V positive of the E<sup>0</sup> for the CO<sub>2</sub>/•CO<sub>2</sub><sup>-</sup> couple. Of course, some of this potential shift is due to the effect of illumination, which could not exceed 1.2 V, based on the bandgap energy for InP. We have proposed that some of this shift is due to adsorption of the CO<sub>2</sub> dimer radical anion, with the strength of the adsorption increasing with increasing negative potential. This appears to be one way to explain the great enhancement of the process with either potential or pressure. If the simple radical anion •CO<sub>2</sub><sup>-</sup> were the adsorbing species, it would tend to be displaced at more negative potentials due to the competitive adsorption of electrolyte cations.

## Concluding Remarks

It seems clear that CO<sub>2</sub> can be reduced both electrochemically and photoelectrochemically at high current densities and at reasonable potentials. We would like to encourage anyone interested in these results to try to improve upon them in every conceivable fashion. We hasten to point out that a broad range of approaches needs to be pursued, including the most basic, innovative ones. However, we believe that the whole field

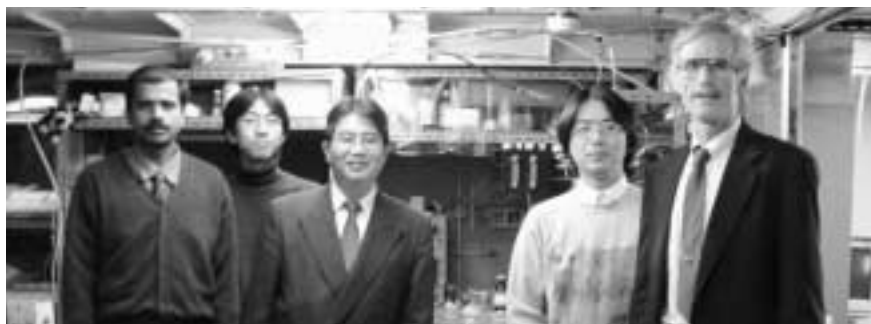


FIG. 5. The CO<sub>2</sub> Busters in the authors' laboratory: from left to right, Dr. Tata N. Rao, Mr. Tsuyoshi Fujii, Professor Akira Fujishima, Mr. Toshio Yamamoto, and Professor Donald A. Tryk.

will be energized by the rapid development of practical technology, with the first steps involving devices that can be compared with other types of existing technology for CO<sub>2</sub> conversion to either fuels or chemicals. In the meantime, let us do our part and save a little energy today, or even better, plant a tree!

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**Akira Fujishima** has been a Professor in the Department of Applied Chemistry at the University of Tokyo since 1986. He is the author of over 500 original research publications and over 20 book chapters and books. He has recently received major awards from the Electrochemical Society of Japan, the Chemical Society of Japan, and the Federation of Asian Chemical Societies. His interests include photoelectrochemistry, photocatalysis, photofunctional materials and diamond electrochemistry, as well as CO<sub>2</sub> reduction.