

in support of the vesicle hypothesis of synaptic transmission, since they show that impaired transmission is associated with loss of vesicles.

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#### References and Notes

- C. A. G. Wiersma, in *The Physiology of Crustacea*, T. H. Waterman, Ed. (Academic Press, New York, 1961), vol. 2, p. 205.
- J. Dudel and S. W. Kuffler, *J. Physiol. London* **155**, 514 (1961).
- B. Katz, *Nerve, Muscle, and Synapse* (McGraw-Hill, New York, 1966).
- K. Uchizono, *Nature* **214**, 833 (1967); K. Kosaka, *Jap. J. Physiol.* **19**, 160 (1969).
- H. L. Atwood and W. A. Morin, *J. Ultrastruct. Res.* **32**, 351 (1970).
- J. Dudel and S. W. Kuffler, *J. Physiol. London* **155**, 543 (1961); H. L. Atwood, *Experientia* **24**, 753 (1968).
- H. L. Atwood, *Nature* **215**, 57 (1967); G. D. Bittner, *J. Gen. Physiol.* **51**, 731 (1968).
- R. G. Sherman and H. L. Atwood, *Science* **171**, 1248 (1971).
- P. C. Caldwell, *J. Physiol. London* **152**, 545 (1960).

- W. F. Loomis and F. Lipmann, *J. Biol. Chem.* **173**, 807 (1948); E. C. Slater, in *Metabolic Inhibitors*, R. M. Hochster and J. H. Quastel, Eds. (Academic Press, New York, 1963), p. 503.
- A. van Harreveld, *Proc. Soc. Exp. Biol. Med.* **34**, 428 (1936).
- A. Takeuchi and N. Takeuchi, *J. Physiol. London* **170**, 296 (1964).
- R. I. Birks and M. W. Cohen, *Proc. Roy. Soc. Ser. B* **170**, 381 (1968); *ibid.*, p. 401.
- A. L. Lehninger, E. Carafoli, C. S. Rossi, *Advan. Enzymol. Relat. Subj. Biochem.* **29**, 259 (1967); J. M. Godfraind, H. Kawamura, K. Krmjevic, R. Pumain, *J. Physiol. London* **215**, 199 (1971).
- J. I. Hubbard and S. Kwanbunbumpen, *J. Physiol. London* **194**, 407 (1968); S. F. Jones and S. Kwanbunbumpen, *Life Sci.* **7**, 1251 (1968).
- R. I. Birks, *J. Physiol. London* **216**, 26P (1971).
- G. D. Bittner and D. Kennedy, *J. Cell Biol.* **47**, 585 (1970).
- R. R. Hoy, G. D. Bittner, D. Kennedy, *Science* **156**, 251 (1967); R. R. Hoy, *J. Exp. Zool.* **172**, 219 (1969).
- E. Holtzman, A. R. Freeman, L. A. Kashner, *Science* **173**, 733 (1971).
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## Unseparated Rare Earth Cobalt Oxides as Auto Exhaust Catalysts

Since Meadowcraft (1) reported that strontium-doped LaCoO<sub>3</sub> was comparable to platinum as an oxygen electrode, the testing of the catalytic activity of LaCoO<sub>3</sub> on certain gas systems has been pursued by our group (2) and others (3, 4). In our study, this particular rare earth cobalt oxide again had activity which rivaled platinum. Also, earlier work by Broyde (5) showed that certain rare earth tungsten bronzes were active as fuel cell catalysts. Consequently, the compound was suggested as a candidate for auto exhaust catalysis. As a next step, cobalt oxides with other rare earths have been prepared, and their catalytic activities have been compared. Little difference between them has been found. This result suggested that a catalyst, just as effective, could be made from the unseparated rare earths with substantial cost savings. Tests with the rare earth mixture as mined did give equally satisfactory results.

The tests were made with a gas mixture of hydrogen (98.82 percent by volume) and *cis*-2-butene (1.18 percent by volume) at a total pressure of 1 atm. The compounds were prepared by firing in air at 1000°C for approxi-

mately 24 hours and then were ground in a ball mill. To be certain that the firing process was complete, we checked the x-ray diffraction patterns of the products for significant peaks from the reactants. Samples (1 to 4 g) of the powders were supported on a glass

wool plug in a Pyrex tube (0.8 cm in diameter) and subjected to a flow rate of the test gas at some 15 cm<sup>3</sup>/min. Various temperatures were used beginning at 100°C and progressing to 400°C; the composition of the emergent gas was determined on a 6-m gas chromatographic column ( $\beta,\beta'$ -oxydi-propionitrile) with a flame ionization detector. The surface areas of the powders before catalysis were measured by the BET (Brunauer-Emmet-Teller) method with N<sub>2</sub>.

The data obtained are given in Table 1. For each rare earth cobalt oxide the temperatures (°C), weight of sample (g), surface area (m<sup>2</sup>/g), and contact time (seconds) are shown. The samples were freshly oxidized in air.

Hightower (4), using a "reduced" LaCoO<sub>3</sub> which had been heated in H<sub>2</sub> at 420°C for several hours, found little methane even at 419°C, the main products being the isomers and *n*-butane. Our earlier results (2) were similar. In our tests, water was observed to form at temperatures 300°C and above, so some reduction was occurring. Thus it seems that the strong hydrogenolysis reaction to produce methane, ethane, and propane which begins at about 300°C probably is associated with the oxidized state of the catalyst. Further investigation is needed to clarify this point. In the proposed use as the oxidation catalyst for auto exhaust this effect should be minor.

Our main conclusion is that the three

Table 1. Catalytic activity of rare earth cobalt oxides. The test gas was H<sub>2</sub> with 1.2 percent (by volume) *cis*-2-butene; the pressure was 1 atmosphere. The composition of the hydrocarbon was: 96.7 percent *cis*-2-butene (c-2); 3.1 percent *trans*-2-butene (t-2); 0.1 percent 1-butene (b-1); 0.1 percent *n*-butane (n-b).

T (C°)	Percentage of feed hydrocarbon converted to product							
	$\Delta$ c-2	$\Delta$ t-2	$\Delta$ b-1	$\Delta$ n-b	$\Delta$ propane	$\Delta$ ethane	$\Delta$ methane	$\Delta$ other
<i>LaCoO<sub>3</sub></i> —1.23 g of 2.86 m <sup>2</sup> /g; 5.0 seconds contact								
400	-95.8	-3.1	-0.1	0.9	0.1	0	97.7	
300	-94.3	-2.9	0	12.9	1.7	3.8	78.3	
200	-3.5	1.7	0.8	0.7	+	+	0.1	*
<i>NdCoO<sub>3</sub></i> —1.36 g of 1.4 m <sup>2</sup> /g; 7.3 seconds contact								
400	-95.6	-3.1	-0.1	2.8	0	0	95.8	
300	-87.1	-0.5	0.6	11.1	4.2	+	71.7	†
200	-4.3	2.3	1.0	0.9	0	0	0	
<i>DyCoO<sub>3</sub></i> —1.91 g of 0.52 m <sup>2</sup> /g; 7.0 seconds contact								
400	-95.8	-3.0	-0.1	0.8	0	0	97.8	
300	-94.4	-2.4	0	10.1	1.5	5.3	80.4	††
200	-9.7	3.8	1.5	4.2	0	0	0	
<i>RCoO<sub>3</sub></i> —1.17 g of 171 m <sup>2</sup> /g; 4.0 seconds contact								
400	-95.3	-3.0	-0.1	0.2	0	0	96.8	†
300	-92.1	-1.6	0.4	3.8	0.8	3.7	83.5	††
200	-3.3	1.5	0.4	1.0	+	+	0.1	

\* Trace C<sub>2</sub>H<sub>4</sub>. † Trace *n*-pentane. †† Trace isobutane.

pure rare earth compounds, DyCoO<sub>3</sub>, NdCoO<sub>3</sub>, and LaCoO<sub>3</sub>, are strikingly similar to each other and to RCoO<sub>3</sub> where R (6) is the natural rare earth mixture as mined.

We suggest, therefore, that the un-separated rare earth oxides can be used to make a cheap auto exhaust oxidation catalyst.

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#### References and Notes

1. D. B. Meadowcroft, *Nature* **226**, 847 (1970).
2. W. F. Libby, *Science* **171**, 499 (1971).
3. G. L. Bauerle, N. T. Thomas, K. Nobe, private communications.
4. W. R. Cares and J. W. Hightower, private communication.
5. B. Broyde, *J. Catal.* **70**, 13 (1968).
6. R is a mixture of rare earths consisting of 49 percent Ce, 33 percent La, 13 percent Nd, and 4 percent Pr oxides; all other rare earth oxides together contribute less than 2 percent. The percentages are by weight.
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## Passive Ventilation in Benthic Annelids?

Vogel and Bretz (1) have recently suggested that passive ventilation is of respiratory importance to burrowing intertidal worms, and that the spontaneous rhythmic bursts of irrigation activity so widespread in the group serve some sort of function in burrow maintenance. They propose that boundary effects of water currents flowing past burrow openings result in the passive flow of water through the burrow, which serves to furnish oxygen to the animal. They suppose that the active pumping of water through the burrow may serve to maintain such burrow structures as the head shaft by preventing the excessive packing of the sandy sieve that fills it. We would like to point out that existing knowledge of ventilatory behavior in annelids does not support these arguments, that annelid pumping activity clearly serves a respiratory function, and that passive flow can be of little importance to annelids.

First, in the cases examined (2), the oxygen consumption of worms in tubes parallels exactly the spontaneous irrigation activity recorded and observed when the animals are in their tubes or burrows. There is a low rate of oxygen consumption during rest and a rapid uptake during bursts of burrow irrigation. The increased oxygen uptake is greater than that required to reoxygenate the small volume of water remaining in the tube at the onset of pumping activity, and bursts of activity last for much longer periods than would be required to flush the burrow (2, 3). During the pumping, the organs of gas exchange are ventilated and the respiratory pigment is oxygenated (2).

Moreover, a respiratory function has been demonstrated directly by measurement of a lower oxygen content in the excurrent than in the incurrent stream generated by spontaneously irrigating worms (4). And the surprisingly high velocities of currents generated by annelids suffice to account for their respiratory needs (2-5).

Although spontaneous rhythmic irrigation in annelids was originally characterized from a closed system (6), several more recent studies have been made of animals placed in moving seawater (3, 5), and one very ingenious investigation on *Arenicola marina* was conducted in the worm's natural habitat (7). Therefore, both active pumping and its cessation occur in the presence of water current flow overhead.

Second, when *Arenicola* [the example cited by Vogel and Bretz (1)] is resting in its burrow between bursts of pumping activity, its body shortens and thickens, effectively plugging the burrow (8) and thus making passive flow by any mechanism impossible. The same is true of *Glycera dibranchiata* (2), several species of *Clymenella* (3), *Amphitrite ornata*, and many other sedentary species. The ventilation current in infaunal worms is often generated by the progression of peristaltic waves of muscular contraction in either direction, with the direction dependent upon the orientation of the worm. Distortion of the body is usually restrained by the walls of the tube or burrow, and hence the action of pumping also occludes the burrow along the length of the shaft. Although passage of peristaltic waves ceases during rest, local contractions of the longitudinal muscles are

sustained, thus maintaining the points of contact when the worm is not physically plugging the whole diameter of the burrow.

A different mechanism of generating currents is employed by errant species, but the habit of most of these worms violates the physical requirements mentioned by Vogel and Bretz (1). Indeed, epifaunal quill worms of the genus *Hyalinoecia* actively prevent passive flow through their tubes by constructing one-way valves at either end (9).

Perhaps most important, it is not clear that passive ventilation would be quantitatively important for any aquatic animal that actively generates currents. Although the mechanism may be applicable to sponges and other groups, its significance must be assessed on the basis of its magnitude. In any event, it is clearly inapplicable to annelids. The respiratory function of irrigation activity has been demonstrated, and resting worms plug their burrows and prevent passive flow through them.

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#### References and Notes

1. S. Vogel and W. L. Bretz, *Science* **175**, 210 (1972).
2. C. P. Mangum and C. Sassaman, *Comp. Biochem. Physiol.* **30**, 111 (1969); R. J. Hoffmann and C. P. Mangum, *ibid.* **36**, 211 (1970); C. P. Mangum, *Amer. Sci.* **58**, 641 (1970); J. A. Carhart, unpublished data on the gas content of *Glycera dibranchiata* coelomic fluid at various external oxygen levels.
3. C. P. Mangum, *Comp. Biochem. Physiol.* **11**, 239 (1964); — and D. M. Miyamoto, *Mar. Biol.* **7**, 7 (1970).
4. R. P. Dales, in *Chemical Zoology*, M. Florkin and B. T. Scheer, Eds. (Academic Press, New York, 1969), vol. 3, chap. 3.
5. G. P. Wells and R. P. Dales, *J. Mar. Biol. Ass. U.K.* **29**, 661 (1951); R. P. Dales, *Physiol. Zool.* **34**, 306 (1961); C. P. Mangum, S. L. Santos, W. R. Rhodes, *Mar. Biol.* **2**, 33 (1968).
6. G. P. Wells, *Nature* **144**, 940 (1939).
7. F. Krüger, *Helgoländer Wiss. Meeresunters.* **11**, 70 (1964).
8. G. P. Wells, *J. Mar. Biol. Ass. U.K.* **28**, 447 (1949).
9. A. T. Watson, *Proc. Trans. Liverpool Biol. Soc.* **17**, 303 (1903).

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We agree with Hoffman and Mangum that for any species the significance of passive ventilation will be evident only upon determination of the magnitude of the phenomenon and its energetic benefits. We plan to make such measurements on one or more polychaetes and hope that other investigators will do so also.