A chemical approach to carbon dioxide reduction without protons

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"Addressing the Mars ISRU Challenge" Keck Institute for Space Studies Workshop
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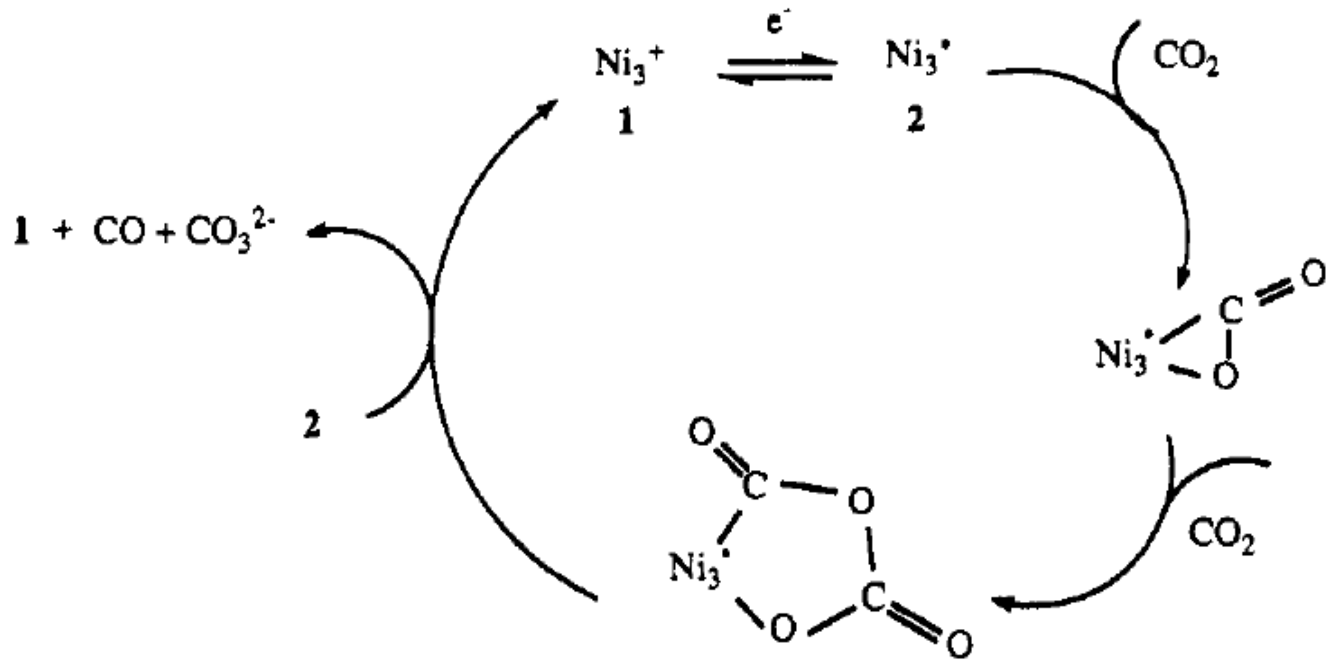
CO_2 reduction mechanism



Ratliff et al., Organometallics, 1992,11, 1988-1990

Splitting CO_2 without water

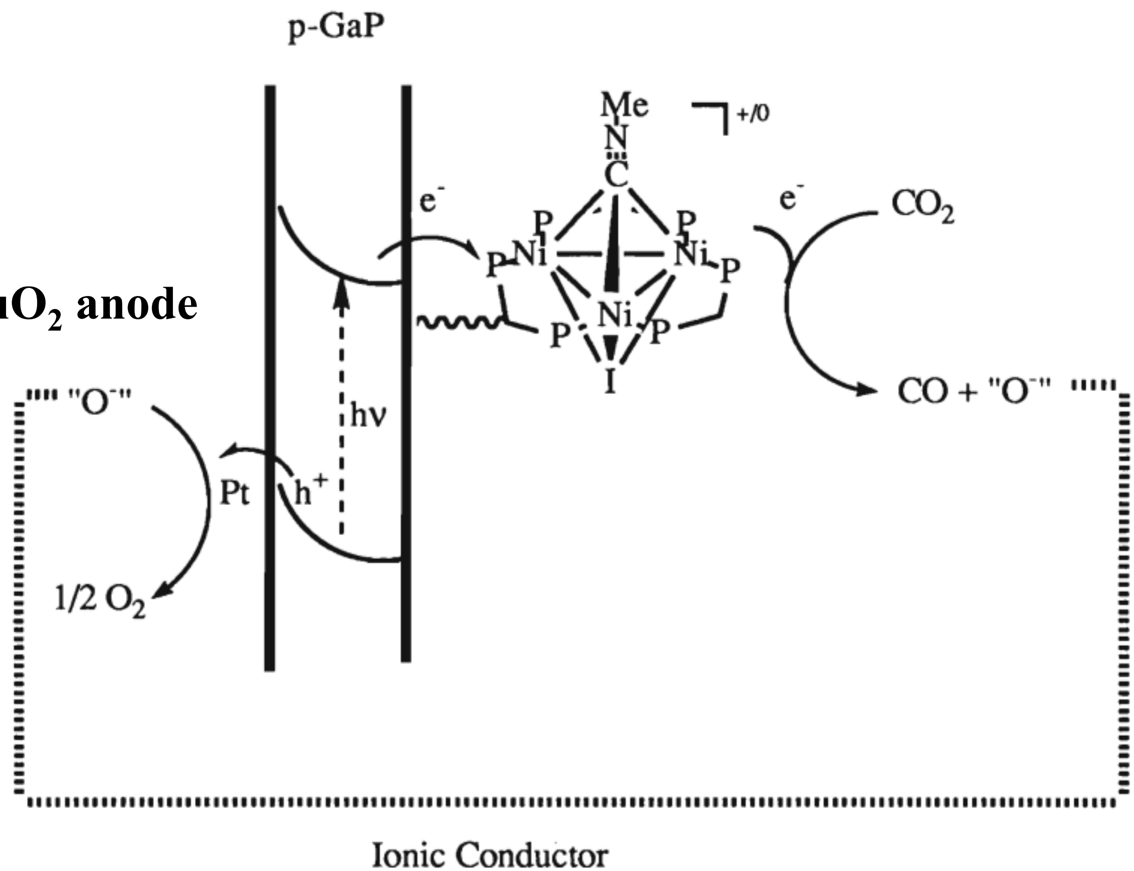
Cathode: $2\ CO_2 + 2\ e^- = CO + CO_3^{2-}$

Anode: $CO_3^{2-} - 2\ e^- = CO_2 + \frac{1}{2}\ O_2$

Net: $CO_2 = CO + \frac{1}{2}\ O_2$

Photoelectrochemical system for splitting CO_2

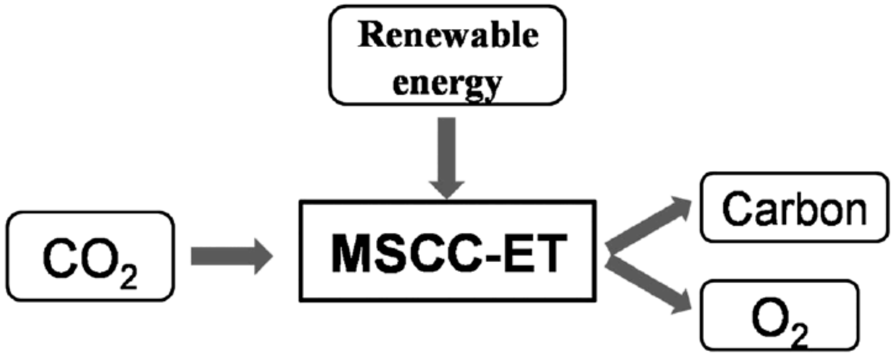
Pt or RuO_2 anode



Net Reaction: $$CO_2 \xrightarrow[\text{p-GaP/Ni}_3\text{/Pt}]{h\nu} CO + 1/2\ O_2$$

Lewis J. *et al*., Resources of near-earth space. The University of Arizona Press, 1993.Pages 799-818.

Molten salts (carbonates) electrolysis



Li_2CO_3 – Na_2CO_3 – K_2CO_3 melts at 500 °C, 2.0 – 5.0 V

$$CO_3^{2-} + 4e^- = C + 3O^{2-}$$

$$C_{(n+1)}O_{(2n+3)}^{2-} + 4e^- = C + nCO_3^{2-} + 3O^{2-}$$

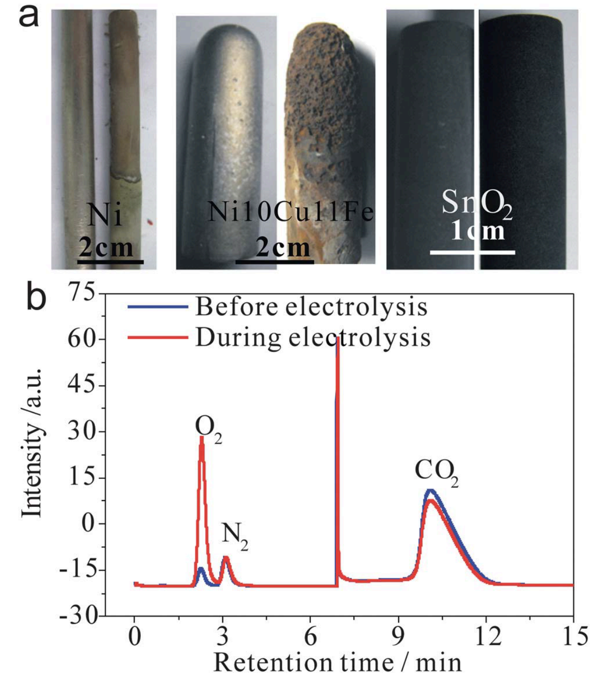
$$O^{2-} + CO_2\,(g) = CO_3^{2-}$$

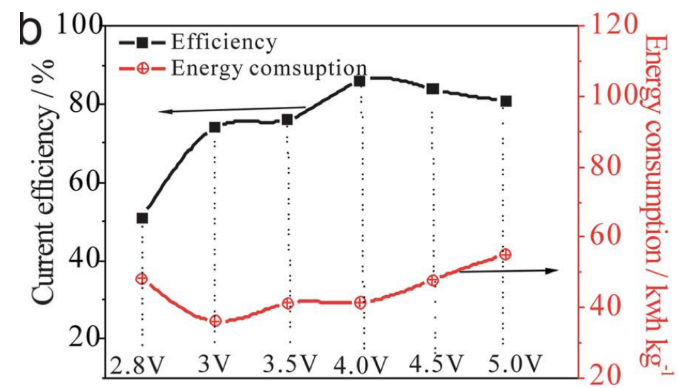
$$CO_3^{2-} + CO_2\,(g) = C_2O_5^{2-}$$

$$CO_3^{2-} + nCO_2\,(g) = C_{(n+1)}O_{(2n+3)}^{2-}$$

$$O^{2-} - 2e^- = 0.5O_2\,(g)$$

$$C_{(n+1)}O_{(2n+3)}^{2-} - 2e^- = (n+1)CO_2(g) + 0.5O_2\,(g)\ (n \geq 0)$$

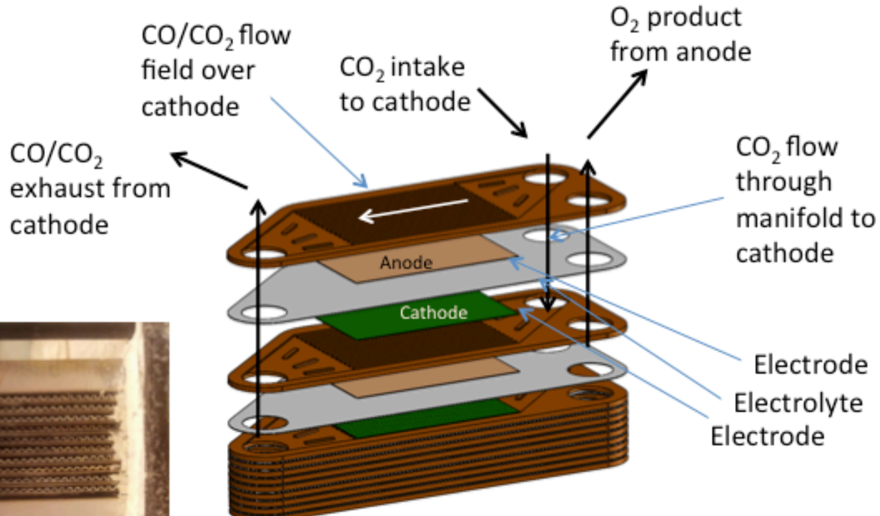




Yin *et al*., Energy Environ. Sci., 2013, 6, 1538-1545

“ MOXIE” - The Mars Oxygen ISRU Experiment

Solid ceramic oxides electrolysis



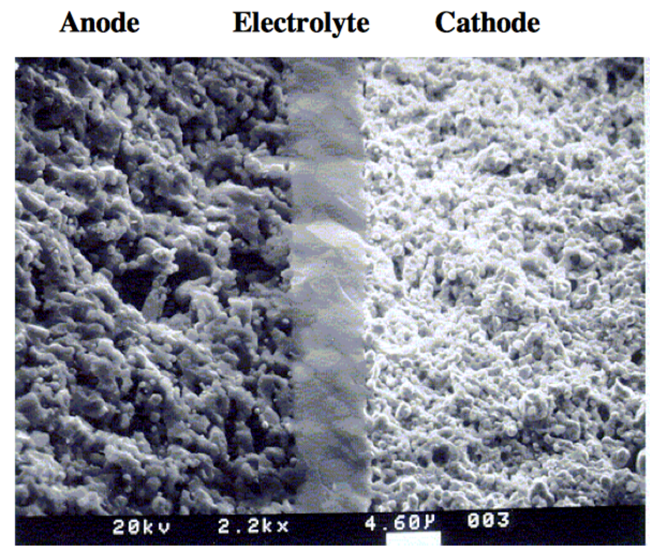


Figure 2. Micrograph of fracture surface of zirconia cell. Anode is a mixture of strontium-doped lanthanum manganite and zirconia. Cathode is a mixture of platinum and zirconia.

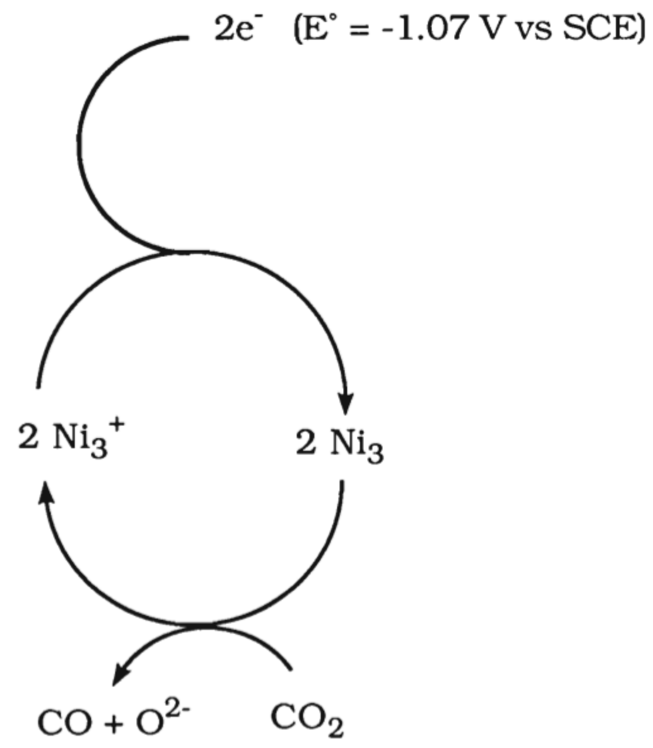
800–850°C range.

Carbon Dioxide Utilization on Mars

Electrocatalytic splitting of CO_2 using Ni cluster catalyst

Solvent selection:

Solvent	Freezing temp., ºC
Acetonitrile	- 46
THF	- 108
DCM	- 97
Acetone	-95
Diethyl ether	-116
Ethanol	-114
Methanol	- 98



Lewis J. *et al*., Resources of near-earth space. The University of Arizona Press, 1993.Pages 799-818.

Kubiak group at UC San Diego

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NASA

“Addressing the Mars ISRU Challenge” Keck Institute for Space Studies Workshop Mission Statement:

To determine the viability of a system that includes photoelectrochemical or electrochemical reduction of CO_2 to convert the available materials and energy resources on Mars to sustain a robotic and human presence with a minimum of imported resources.