Electrochemical Conversion of Carbon Dioxide to Methane by Depolarized Anode Alkaline Membrane CO₂ Electrolizer (DAAM-CE)

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State of the art.
The conversion of carbon dioxide to fuels or chemical feedstock represents an attractive issue to control the levels of atmospheric carbon dioxide and to promote energy storage. This conversion if carried out using electrical energy from renewable sources could yield to "carbon neutral fuels". In other words this kind of process mimics energy storage by nature using the photosynthesis way in green plants and microorganisms. Previous studies on CO₂ reduction were focused on the use of alkaline solution electrolytes, porous separators and solid metal-based electrode structures. There are known various advantages to use a cell configuration based on a solid polymer ion-conducting membrane electrode assembly (MEA) with supported catalytic electrodes and these benefits are well-recognized in the fuel cell field. Concerning the use of polymer electrolyte-based CO₂ electrolysis cell, there is available an early Technical Report (LaConti et al. 1986) from United States Technologies Corp.; otherwise the use of a membrane electrolyte cell configuration in CO₂ reduction has been a more recent issue.

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In the course of previous studies of electrocatalysts for Alkaline Direct Alcohol Fuel Cells (ADAFCs), we have discovered that nanosized Pd particles, alone or promoted by Ni-Zn phases, promote selectively the partial oxidation of (poly)alcohols to the corresponding (poly)carboxylate in alkaline environment [1]. Figure 1a shows a simplified working scheme of a direct ethanol fuel cell (DEFC) where ethanol (CH₃CH₂OH) is selectively converted into acetate (CH₃COO⁻) and the electrolyte is an anion-exchange membrane. Ethanol is oxidized on the anode to acetate according to following equation, releasing four electrons that are utilized to reduce one oxygen molecule to four OH⁻ groups on the cathode. Efficient devices of this type have been recently developed for other renewable polyalcohols such as ethylene glycol and glycerol [2,5].

C₂H₅OH + 5 OH⁻ → CH₃COO⁻ + 4 H₂O + 4 e⁻
anode  E°₁ = -0.72 V

Taking into account these studies we are studying the CO₂ electroreduction to hydrocarbons (i.e. CH₄) at the cathode compartment by the use of a technology named DAAM-CE (Depolarized Anode Alkaline Membrane CO₂ Electrolizer) in order to design and realize the following new concept: an electrochemical reactor for the production of both "Fuel at the cathode and value-added chemicals". In other words: an hydrocarbon fuel (i.e. CH₄) is produced on the cathode side from CO₂ reduction; on the anode side, an aqueous alcohol solution (i.e. ethanol) in conjunction with a Pd-based electrode, lead to the corresponding carboxylate product (i.e. acetate) instead of O₂ gaseous product.

Research group supporting references