Technology Summary: Composite Electrode Material for Electrochemical Synthesis of Dimethyl Carbonate

Opportunity Statement

Due to its unique properties and its status as one of the few VOC-exempt solvent approved by the EPA, Dimethyl Carbonate (DMC) is able to find applications in a wide range of products.
The main applications and markets for DMC are:

1. **Production of polycarbonate**
   Polycarbonate (PC) is an amorphous, thermoplastic and transparent plastic. Current annual production of polycarbonates amounts to two million tons worldwide and expected to increase about 5-10% annually **(Ref [1],[2]).** At present, PC is made mainly by a phosgene-based technique. Phosgene is highly toxic and considered a serious pollutant. DMC can provide an environmentally attractive alternative to Phosgene in this market.

2. **Synthesis of Isocyanates**
   DMC is one of the raw materials used for synthesis of isocyanates, which include MDI (diphenylmethane diisocyanate), HDI (hexamethylene diisocyanate) and TDI (toluene diisocyanate). These isocynantes are used to produce a wide range of material including polyurethane, coating material and insecticides. According to market reports **(Ref [3])**, the demand for polyurethane resin in US was 7.6 billion pounds in 2009, driven by opportunities in building insulation, coatings and adhesives.

3. **Fuel additive**
   DMC is a potential replacement for ethanol as a fuel additive. According to a report by University of Bari, demand for DMC as a gasoline additive is potentially 30 million tons per year. **(Ref [4],[5])**

4. **Electrolyte for Lithium-ion battery**
   DMC can be used as a solvent in the manufacturing of electrolytes in lithium ion batteries. **(Ref [6],[7])** With the expected mass adoption of electric vehicles in the near future, demand for DMC as a raw material for lithium ion electrolyte is expected to rise rapidly.

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Current technologies for manufacturing DMC include the following:

1. **Phosgene Method**
   This is the traditional method for DMC manufacture. Under this method, methanol is reacted with phosgene in the presence of 15–50 wt. % aqueous alkali metal hydroxide solution and an inert, water-immiscible organic solvent. The reaction is carried out at temperatures ranging from -20°C to 40°C. The key disadvantage of this process is the formation of hydrogen chloride, an extremely corrosive compound, and the use of phosgene, a highly toxic gas.

2. **Oxidative carbonylation method (Ref [8])**
   Oxidative carbonylation method is extensively used for synthesis of DMC. Under this method, methanol oxidative carbonylation reaction is carried out in the presence of oxygen and a catalyst by using carbon monoxide as a raw material. The drawback of this process is the high cost associated with the use of carbon monoxide as a raw material and management of corrosion associated with the carbon monoxide reaction.

3. **Direct synthesis of DMC from CO_2 and methanol**
   This is an area of research that has received increased attention in recent years.(**Ref [9]**) Under this method, CO_2 is reacted with methanol, with the reaction usually carried out in the presence of a catalyst, which assists in the activation of CO_2. This is considered one of the most desirable processes for DMC manufacture as there are few by-products and CO_2 is easily available. However, the challenge in implementing this process is that the catalyst and the process conditions required result in significant cost increase for the process.

Problem

In light of the disadvantages associated with these production methods, the direct synthesis method is growing in popularity. The method uses cheap and easily available raw materials, such as CO_2 and methanol, and the resulting by-products are also less harmful to the environment. However, the catalysts used to activate CO_2 are difficult to prepare and regenerate, and can be deactivated by the water generated during the process.

Therefore, there is a need for a solution that takes advantage of the benefits of the direct synthesis method to produce DMC and yet overcomes its current shortfalls.

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360ip Partner's Solution

360ip Partner's invention relates to a novel composite electrode with exceptional catalytic activity that can be used to synthesize DMC from CO_2 and methanol at normal process conditions without the use of a catalyst.

The production of DMC using this technology involve two main steps

1. Preparation of composite electrode, and 2. Electrolysis process.

1. Preparation of composite electrode

The composite electrode is a combination of transition metal nanoparticles and a conductive polymer. The preparation of the composite electrode material includes the following steps:

1.1 Preparation of transition metal nano particles

Transition metal nanoparticles are obtained from transition metals, such as iron, cobalt, platinum, silver, gold, vanadium, nickel, copper, iridium and molybdenum. They are obtained using a liquid-phase reduction method from the metal salt solution.

1.2 Chemical polymerization

Under the chemical polymerization process, metal nanoparticles are mixed with monomers. Oxidants such as ammonium persulphate, potassium dichromate and hydrogen peroxide are used for oxidizing and polymerizing monomers to form conductive polymers. The composite material obtained is used as an electrode in DMC production.

The weight ratio of transition metal nanoparticles to conductive polymers in the composite electrode is in the range of 0.01–0.1:1.

2. Electrolysis process

The prepared composite electrode is then used for CO_2/methanol electrochemical synthesis of DMC. The electrochemical synthesis is performed using the following steps:

a. Placing the composite electrode as a cathode in an electrolysis tank containing magnesium, aluminum or zinc as a sacrificial anode and imidazole ionic liquid as electrolyte;

b. Introducing CO_2 for electrolysis up to 5–10 hours at a constant current of 5–20 mA/cm^2 and a temperature of 30–70 ºC;

c. Adding methanol after completion of electrolysis; and

d. Separating products after distillation.

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Benefits

360ip Partner's technology has the following benefits:

- Facilitates high reactivity of CO_2 and effective utilization of CO_2 resources.
- Overcomes difficulties in preparation and regeneration of catalysts and high pressure requirements of conventional DMC synthesis.
- Low-cost process given that the raw materials are inexpensive and easily available.
- No harmful byproducts/gases, such as hydrogen chloride and polyol, are released.
- Avoids corrosion of equipment unlike conventional phosgene and oxidative carbonylation processes.

Patents

360ip's Partner has filed one patent application on this invention and plans to seek protection in multiple jurisdictions.

360ip is seeking interested parties for licensing, further development and commercialization of this technology-based solution.

For additional information, contact:
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