POSTERS
Experimental investigation on CO₂ methanation process for solar energy storage

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Introduction

The utilization of the captured CO₂ as a carbon source for the production of energy storage media offers a technological solution for overcoming crucial issues in current energy systems. Solar energy production generally does not match with energy demand because of its intermittent and non-programmable nature, entailing the adoption of storage technologies. Hydrogen constitutes a chemical storage for renewable electricity if it is produced by water electrolysis and is also the key reactant for CO₂ methanation (Sabatier reaction). The utilization of CO₂ as a feedstock for producing methane contributes to alleviate global climate changes and sequestration related problems. The produced methane is a carbon neutral gas that fits into existing infrastructure and allows to overcome issues related to the aforementioned intermittency and non-programmability of solar energy.

In this paper an experimental apparatus, composed by PV panels, an electrolyser and a tubular fixed bed reactor is built and used to produce methane via Sabatier reaction. The objective of the experimental campaign is the evaluation of the process performance and the comparison with other CO₂ valorization paths.

Methane and methanol production process

The two processes are shown in their schematic configuration, in which are represented topological components of the production apparatus.

Materials and methods

Experimental apparatus

The experimental apparatus includes the following sections: an electrolyser, CO₂/O₂ mixing section, heating section, Sabatier reactor and a water separation section.

Experimental procedure

Hydrogen is produced by an electrolyzer, then it is mixed with CO₂ according to the stoichiometric proportion. Gas flows are controlled by flowmeters. The gaseous mixture flows through the two cameras; the first one constitutes the preheater section, while the second is the Sabatier reactor. The reactor is filled with Ni catalyst pellet, necessary for reaction development (it permits to improve the kinetics of the reaction). The reactor is equipped with one pressure sensor and one temperature sensor (type K thermocouple). For reducing heat loss and for safety reasons, the two cameras are coated with thermo-insulating material.

Experimental runs

The experimental campaign consists of 14 tests. The difference between one test and the other lies in the variation of four main parameters: CO₂/H₂ ratio, flow conditions, temperature and pressure. Values adopted for these parameters are shown in the following table.

<table>
<thead>
<tr>
<th>CO₂/H₂ ratio</th>
<th>Flow conditions</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low</td>
<td>250</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>High</td>
<td>200</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Medium</td>
<td>150</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Low</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>High</td>
<td>50</td>
<td>25</td>
</tr>
</tbody>
</table>

Experimental tests were carried out with internal temperature in the optimal range from 250 °C to 451 °C and an internal pressure from 2 bar to 20 bar. Tests from 1 to 10 were carried out using the stoichiometric CO₂/H₂ ratio (1/4), while tests from 11 to 14 with ratio equal to 1. Only tests 7-10 were realized in batch condition. For each test, the composition of the gaseous mixture collected at the end of the process is shown.

Experimental results show that the ratio between the spent energy and the stored energy is higher for the methanol process. The methane production process has a better performance in terms of energy storage capability.

Discussion

Results allow to discuss the influence of the operating parameters on the methanation process. The in-continuous operation of the apparatus is clearly the fundamental element to obtain noteworthy results. Tests 11-14 demonstrated the strong conversion decrease caused by a deviation from the ideal value of the CO₂/H₂ ratio. Third place of importance is occupied in the tests CO. Of the experiments, CO₂ was converted with Ni catalyst. CO₂ is catalysed with Ni catalyst, resulting in the following reaction:

\[ \text{CO}_2 + \frac{1}{2} \text{H}_2 \rightarrow \text{CH}_4 + \frac{1}{2} \text{H}_2 \text{O} \]

The reaction is exothermic and is limited by the thermodynamic equilibrium. Operating temperatures are typically around 250-400 °C.

Materials

Sabatier reaction is catalysed by Ni-based catalyst containing oxide NiO. It has to be converted into the active form for the methanation reaction. Activation is achieved by the following process. At the beginning pure nitrogen is flowed inside the reactor at 1.5 bar, in order to remove air present into the reactor. The internal temperature is brought to 220 °C with a rate of 60 °C/h. Then pure hydrogen is flowed at 2 bar and the system is heated to 430 °C with a gradient of 120 °C/h.

Comparison between methane and methanol production process

The experimental methane-based process was compared to the methanol-based process on the basis of the ratio: Spent Energy/Stored Energy. The considered parameter is an adimensional number calculated as the ratio between the specific energy spent in all the sections of the process to produce the fuel in its storing form and the specific energy stored in the fuel.

Results show that the ratio between the spent energy and the stored energy is higher for the methanol process. Methane production process has a better performance in terms of energy storage capability.
1 Introduction
Electret is a dielectric material that has a quasi-permanent electric charge or dipole polarization. An electret generates internal and external electric fields, and it is the electrostatic equivalent of a permanent magnet. Electrets have important technological application from established ones such as microphones or particulate filters to emerging ones as in powering energy harvesting devices. At smaller length scale a localized charge can improve the functionalities of nanostructured materials, providing further transduction schemes for MEMS and NEMS devices. However to guarantee the stability of the polarization in micro systems is challenging. Moreover, the fabrication process can induce significant changes in the structural and mechanical properties. In this work, we study the behavior of SiO₂ nano and microparticles when charged by injecting electrons by field emission scanning microscope (SEM) at energy ranging between 2 and 8 keV.

3 Characterization of the charge by SEM
Shift of Duane-Hunt limit: The charge storage gives rise to a negative surface potential that has the effect to reduce the landing energy of the beam electrons.

\[ E_L = E_0 - e|V_s| \Rightarrow e|V_s| = E_0 - E_L \]

The energy shift can be monitored measuring the continuum x-ray radiation: The energy cut-off of the spectra emitted from the charged region is compared with the energy cut-off of the spectra from a conductor at zero potential (expected to be \( E_0 \) \[3\]).

Electronic spectroscopy: The SEs energy distribution is shifted by the negative surface potential while its shape remains unchanged. \[4\]

Changing the collector voltage \( V_c \) of the E-T detector we can select the energy of collected SEs.

SEs with higher kinetic energy (supplied by \( V_c \)) are detected at higher collector voltage \( V_c \).

5 Time decay of the charge
The charging state can be monitored by using SEM images collected at a much lower beam energy not to alter the pre-existing charge state.

Two decay time constants:
- *fast*
- *slow*

References

2 Charging process and electret fabrication by SEM
To assess the charging process we adopt the Total Yield Approach \[1\],[2]

\[ \delta = \frac{I_{SE}}{I_B} \]
\[ \eta = \frac{I_{BSE}}{I_B} \]
\[ \sigma = \delta + \eta \]

\[ \frac{\partial Q}{\partial t} = (1-\sigma)I_B \]

- There are three charging regions depending on the emission properties of the sample (\( \sigma < 1 \) or \( \sigma > 1 \)).
- At the crossover energy \( E_x \), the sample is uncharged
- Control on penetration depth \( R \propto E_x^{-0.67} \)

Increasing the primary electron energy, we expect to inject the charge deeper and deeper into the bulk of the material, leading the system to greater negative potential.

4 Results
The measured surface potential is plotted as a function of the incident energy, both for 0.5 and 1.0 micron sized particles. We can see that in both cases the potential increases almost linearly at the beginning, until it reaches a maximum value and then become stationary, as there is a saturation due to the leakage and transmitted currents that prevent the dielectric breakdown. The maximum is reached when the penetration depth of the primary electrons is approximately equal to half the diameter of the particles. The measured surface potentials are consistent with those expected considering the dielectric strength of SiO₂.

6 Conclusion
In this work we have analyzed the behavior of micro and nanoparticles of SiO₂ exposed to an energetic electron beam, in order to fabricate electrets with reduced dimensionality. The values of the surface potential, acquired with two independent techniques, have shown that the particles have been charged till to the saturation level. The quite slow time decay allows exploiting them for new technological applications. It is also proved that SEM allows injecting efficiently the charge, and its high resolution allows controlling the penetration and the charging state of nano and micro structured samples.
Piezoelectric ZnO Microstructures: Synthesis and Characterization for Energy Harvesting

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Piezoelectricity is a natural property of certain materials to generate electric potential when they are subjected to mechanical stress. If a straight vertical rod is deflected, a strain field is created as the outer surface is stretched and the inner surface is compressed, resulting in an electric field along the z direction of the structure analysis. It’s possible to estimate mechanical resonance frequency and piezoelectric potential by modeling, with finite element method (FEM), a ZnO microrod as a hexagonal structure and by applying a uniform horizontal force on its top surface (Fig. 1).

With hydrothermal route we obtained microrods on Si substrate and afterwards on IDE (Fig. 2). Solutions containing zinc acetate and HMTA (hexamine) yield rods with diameters of 3 ± 5 µm and lengths that range from 12 to 17 µm. The zinc acetate and HMTA concentrations should be 0.1M and 0.4M and the temperature of laboratory oven must be 85 °C, for 5h.

Characterization

A scanning electron microscopy (SEM) with a field-emission-scanning electron microscope was used to observe the morphologies of ZnO microrods. Light scattering experimental techniques (micro-Raman and micro-Brillouin) were performed in order to estimate elastic and piezoelectric properties of microcrystals. X-Ray Diffraction (Cu Kα, λ = 1.5418 Å) gave us information about orientation of microrods on the substrate. SEM innovative method for piezoelectric characterization has been introduced: two conductive probes on a single crystal could give its mechanical frequency resonance driven by thermal noise.

Conclusion

ZnO microrods obtained by hydrothermal route could be studied to investigate their piezoelectric and elastic properties. Several techniques were used in this work, and a new one has been introduced, by using SEM conductive probes on a single crystal. In the near future we will continue to synthesize this micro materials on IDE with the aim to develop a device for energy harvesting from vibrational noise.

Results

- Light Scattering: Micro-Brillouin (Stiffness matrix elements Tab.1), Micro-Raman (Phonon modes of ZnO Tab.2)
- X-Ray Diffraction (Structure of microrods and their orientations)
- SEM probes on single crystal (Resonance frequency driven by piezoelectric effect and thermal noise)

Acknowledgements
Bu proje kapsamında tıbbişin frekansları, 10 Hz - 30 Hz aralığında olan mekanik tıbbişinin elektrik üretmek için yeni bir elektromanyetik üreticinin tasarlanıp üretilmiştir. Başlangıç olarak; Ansys Maxwell elektromanyetik benzetim paketi ile sistem elektromanyetik modeli geliştirilmiş; yüksek yoğunlukta manet akı oturulmuş bir nüve üzerine Halbach modülü ile göre窟-Speedy mühür miknatıslar yerleştirilmiştir. Sistem genel olarak, doğrusal löyutunun bir nüve yapısının etrafına sarmış bir bobinden enerji üretimi konu almaktır. Nüvecin iki ıç su antenleri ile iyi yarımdan elde edilmiş, bası hamonic hareket oluştururarak elektrik enerjisinin işçilık şekillerde elde edilmiştir. Sistemin sağı çizimlendirilmiş tıbbişin en ucuz formülü düzeltici adı altında hareketin bulunduğu ortamda sürekli güç oturulabilirme yeteneği bulunmaktadır. Bu tıbbiğin durumunda maksimum gücün en ucuz bir parametre olup, \( P_{\text{max}} = 0.3684 \text{ mW/cm}^2 \) değeri üretilen tıbbişin diğer uyguları olarak görülmektedir. Literatürdaki diğer çalışmalarda da kullanılan bu güç çeşitleri, patent başvuruları, en yüksek güçsüz devam etmektedir. Uluslararası konferanslarında da bazı bulguların sunulması olan bu projenin yurt dış yasalar olarak SCI indelikli bir dergiye makale gönderimi yapılıp ölü hakem incelemesindedir.

ÖZET

Seçkil 1(a)’de gösterilen Maxwell 3D benzetim programı modellenmesi yapılmış ve Şekil 1(b)’de gösterilen spazem teorisi sonlu elemanlar yöntemi ile elektromanyetik benzetimlerin yapılmasından bulguların manet akı yoğunluğu (B) teşpit edilmiştir. Nüve ve bobin geometrileri ve elektromanyetik güç, diğer edilen bu tıbbiğin durumunda kararlaştırılmıştır. Nüve üzerine hareket bıçiminde 0.75 T akım yoğunluğuna ulaşılması.

DENEYSEL ÇALIŞMALAR

Deneysel çalışmalarda, hem bu programın yurt dışında ve hem de elektromanyetik modellemede, 3D benzetim programı modellenmesi yapılmış ve Şekil 1(b)’de gösterilen spazem teorisi sonlu elemanlar yöntemi ile elektromanyetik benzetimlerin yapılmasından bulguların manet akı yoğunluğu (B) teşpit edilmiştir. Nüve ve bobin geometrileri ve elektromanyetik güç, diğer edilen bu tıbbiğin durumunda kararlaştırılmıştır. Nüve üzerine hareket bıçiminde 0.75 T akım yoğunluğuna ulaşılması.

**Üretim**, Sınan Akbababa

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**Makale:** “Sonlu Elektromanyetik Sınai Enerji Aletleri, Yenilenebilir Enerji ve Sırpçalanma”

**Sonuçlar ve Literatür**

**Bu projeye yetenekli bir düşük güç enerji üretej akademik ve-sendikeler:**

**Çözüme dair literatürde göz atılmış:**

**Üretim:** Sırpçalanma industriyesi**

**Sırpçalanma:** Sırpçalanma, **Donanım:**

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Underwater piezoelectric energy harvester

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Abstract—In this work we present an energy harvester for underwater applications. It is based on a piezoelectric cantilever and it can be used to harvest energy in water pipelines. We present a finite elements analysis and the experimental results of the tests conducted in a reduced size model of a real pipeline.

I. INTRODUCTION

In this paper we describe how we are powering a sensor to monitor physical and chemical parameters in a water pipeline. In order to provide self-powering capability to wireless sensor devices, we decided to not use batteries but an energy harvester [1, 2]. Generally, a turbine (e.g. Pelton, Darrieus) for capturing the energy of the water flux is used, but we have chosen to exploit the vibrations induced by the Von Karman Vortex [3] generated by turbulence around a cylindrical or blunt body.

Fig. 1 shows a simulation of the vortex that a blunt body generates in a water flux. Self-sustaining drag and transversal lift force are generated by the vortex and after a transient the excitation becomes periodic.

The work done by the vibrating lift force is converted into electricity by using a piezoelectric element. This way to harvest energy presents some advantages versus micro turbines:
- independent from flow direction;
- self-starting and reduced maintenance;
- small reduction of the flow pressure (1/100 bar);
- capacity to avoid solid bodies or particulate present in waste or rain water;
- no need of flow constraint.

II. ENERGY HARVESTER DESIGN

The first version of the water flux energy harvester is based on piezoelectric element, thus we named it Piezoelectric Vortex Generator (PVG). The overall mechanical design of the generator is shown in Fig. 2.

The transduction element is a bimorph piezoelectric beam that is provided by Midé Volture company (www.mide.com, model V21BL). Two piezoelectric layers are deposited on the side of inner steel layer and have copper electrodes on both sides. Then the beam is packaged with FR4 and presents a thickness of 0.8 mm. The mechanical water-air interface is disk-cap printed in ABS. This element has the important function of feedthrough for electrical connections.

This energy harvester works in linear mode and its resonance frequency, when in the water, is about 30 Hz. The excitation due to the water flux is a sinusoidal force at the frequency \( f = \frac{St \cdot v}{d} \), where \( St \) is the Strouhal number [4], \( v \) is the speed of the water and \( d \) is the cylinder diameter. At the speed of 0.7 m/s, this corresponds to a frequency of 6 Hz. Even if the two frequencies are different, we obtained a good conversion confirming that our harvesting is working on a wide band.

III. TEST SETUP

In our lab at NiPS we have built a reduced scale (1:10) water circuit in order to test the energy harvester (Fig. 3). A pump pulls and pushes the water from a reservoir through a 2 inches wide pipeline where we placed the piezoelectric generator (PVG). Smaller flexible tubes (1 inch in diameter, in yellow) connect the test pipeline (in grey) to the pump and to the reservoir creating a closed loop circuit.

The pump is a common one for water. It is made by Lowara, model CEAM 80/5 A. It can provide a flux of 100 ltr/minute, requiring a power of 0.75 kW at 230 Vac. We also provided a power regulator to change the rpm of the pump and the flux of the water.

Our target is to make this system work with a flux of about 100 ltr/s: we can expect much more power in a real scenario. Thus this setup is useful to understand the capability of such kind of energy harvesters.
IV. PRELIMINARY RESULTS

We conducted several tests to evaluate our system. First, we investigated if the water flux was enough to make our generator to oscillate. After this we tried to optimize the depth of insertion of the oscillator in the pipeline. We performed this operation empirically trying to find the maximum output voltage with an oscilloscope.

Finally we evaluated the amount of power that can be converted in a typical working condition where the water flux was travelling at the speed of 0.7 m/s. We loaded the piezoelectric with a variable resistor and we have found that the optimal load value is 300 kOhm. In these conditions the RMS value of the output voltage is approximately 7 V and the corresponding power is about 160 µW.

Fig. 4 depicts the output voltage when the piezoelectric is loaded with a 300 kOhm resistor. As it can be seen, this signal is not sinusoidal. This is due to the impacts of the cylinder on the internal walls of the pipeline.

V. CONCLUSIONS

We have demonstrated an alternative technology to extract energy from a water flux with minimal impact on the pressure in the pipeline (0.01 bar drop).

We have also demonstrated that Von Karman Vortex can be used to make extract energy from a flux by using a piezoelectric and that this energy harvester has a wide frequency response.

The proposed system can be further optimized: e.g. experimenting different shapes of the submersed oscillating body.

We are also working on self-tuning of the mechanical resonance frequency of the energy harvester with excitation: water speed can change and consequently the frequency of the excitation.

ACKNOWLEDGMENTS

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REFERENCES