Materiali nanostrutturati per la produzione di energia ed il suo stoccaggio

mediante elettrocatalisi (Celle a combustibile ed Elettrolizzatori)

Candidata
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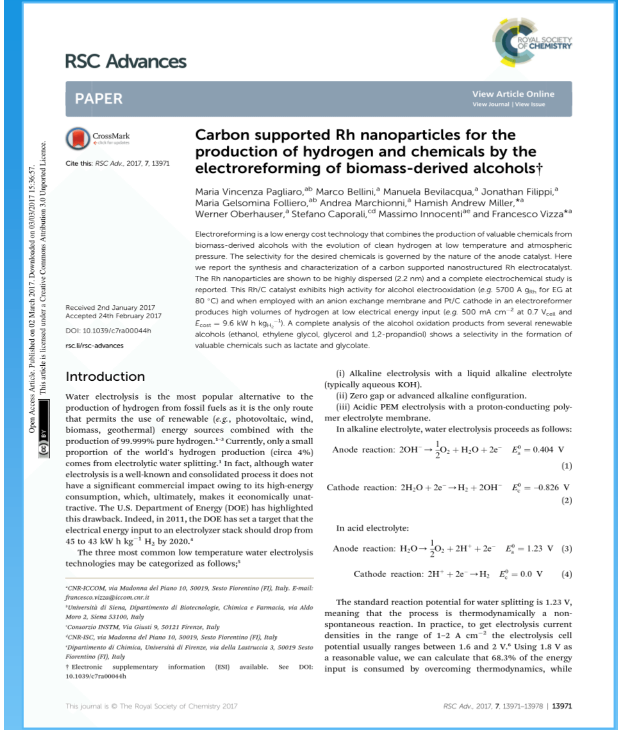
ICCOM

Dipartimento Scienze Chimiche e Tecnologie dei Materiali

Young Investigator Award 2019

Rh



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Carbon supported Rh nanoparticles for the production of hydrogen and chemicals by the electroreforming of biomass-derived alcohols†

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Electroreforming is a low energy cost technology that combines the production of valuable chemicals from biomass-derived alcohols with the evolution of clean hydrogen at low temperature and atmospheric pressure. The selectivity for the desired chemicals is governed by the nature of the anode catalyst. Here we report the synthesis and characterization of a carbon supported nanostructured Rh electrocatalyst. The Rh nanoparticles are shown to be highly dispersed (2.2 nm) and a complete electrochemical study is reported. This Rh/C catalyst exhibits high activity for alcohol electrooxidation (*e.g.* 5700 A g_{Rh} for EG at 80 °C) and when employed with an anion exchange membrane and Pt/C cathode in an electroreformer produces high volumes of hydrogen at low electrical energy input (*e.g.* 500 mA cm^{-2} at 0.7 V_{cell} and $E_{cost} = 9.6$ kW h $kg_{H_2}^{-1}$). A complete analysis of the alcohol oxidation products from several renewable alcohols (ethanol, ethylene glycol, glycerol and 1,2-propandiol) shows a selectivity in the formation of valuable chemicals such as lactate and glycolate.

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Introduction

Water electrolysis is the most popular alternative to the production of hydrogen from fossil fuels as it is the only route that permits the use of renewable (*e.g.*, photovoltaic, wind, biomass, geothermal) energy sources combined with the production of 99.999% pure hydrogen.[1–3] Currently, only a small proportion of the world's hydrogen production (circa 4%) comes from electrolytic water splitting.[1] In fact, although water electrolysis is a well-known and consolidated process it does not have a significant commercial impact owing to its high-energy consumption, which, ultimately, makes it economically unattractive. The U.S. Department of Energy (DOE) has highlighted this drawback. Indeed, in 2011, the DOE has set a target that the electrical energy input to an electrolyzer stack should drop from 45 to 43 kW h kg^{-1} H_2 by 2020.[4]

The three most common low temperature water electrolysis technologies may be categorized as follows;[5]

(i) Alkaline electrolysis with a liquid alkaline electrolyte (typically aqueous KOH).

(ii) Zero gap or advanced alkaline configuration.

(iii) Acidic PEM electrolysis with a proton-conducting polymer electrolyte membrane.

In alkaline electrolyte, water electrolysis proceeds as follows:

$$\text{Anode reaction: } 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \quad E_a^0 = 0.404 \text{ V} \tag{1}$$

$$\text{Cathode reaction: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E_c^0 = -0.826 \text{ V} \tag{2}$$

In acid electrolyte:

$$\text{Anode reaction: } H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \quad E_a^0 = 1.23 \text{ V} \tag{3}$$

$$\text{Cathode reaction: } 2H^+ + 2e^- \rightarrow H_2 \quad E_c^0 = 0.0 \text{ V} \tag{4}$$

The standard reaction potential for water splitting is 1.23 V, meaning that the process is thermodynamically a non-spontaneous reaction. In practice, to get electrolysis current densities in the range of 1–2 A cm^{-2} the electrolysis cell potential usually ranges between 1.6 and 2 V.[6] Using 1.8 V as a reasonable value, we can calculate that 68.3% of the energy input is consumed by overcoming thermodynamics, while

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Pd-CeO2

energies

MDPI

Article

Improving the Energy Efficiency of Direct Formate Fuel Cells with a Pd/C-CeO_2 Anode Catalyst and Anion Exchange Ionomer in the Catalyst Layer

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Abstract: This article describes the development of a high power density Direct Formate Fuel Cell (DFFC) fed with potassium formate (KCOOH). The membrane electrode assembly (MEA) contains no platinum metal. The cathode catalyst is FeCo/C combined with a commercial anion exchange membrane (AEM). To enhance the power output and energy efficiency we have employed a nanostructured Pd/C-CeO_2 anode catalyst. The activity for the formate oxidation reaction (FOR) is enhanced when compared to a Pd/C catalyst with the same Pd loading. Fuel cell tests at 60 °C show a peak power density of almost 250 mW cm^{-2}. The discharge energy (14 kJ), faradic efficiency (89%) and energy efficiency (46%) were determined for a single fuel charge (30 mL of 4 M KCOOH and 4 M KOH). Energy analysis demonstrates that removal of the expensive KOH electrolyte is essential for the future development of these devices. To compensate we apply for the first time a polymeric ionomer in the catalyst layer of the anode electrode. A homopolymer is synthesized by the radical polymerization of vinyl benzene chloride followed by amination with 1,4-diazabicyclo[2.2.2]octane (DABCO). The energy delivered, energy efficiency and fuel consumption efficiency of DFFCs fed with 4 M KCOOH are doubled with the use of the ionomer.

Keywords: direct alcohol fuel cells; formate; alkaline membrane; palladium; ceria; ionomer; energy efficiency

1. Introduction

Direct Formate Fuel Cells (DFFCs) are attractive power sources because as a fuel formate salts have specific advantages compared to alcohols like methanol and ethanol [1]. Formate salts can be easily stored, transported, and handled in their solid state and can be combined with water to form a liquid fuel solution [2]. Worldwide production of its precursor formic acid is around 7.2×10^5 t·y^{-1}. Although industrial production involves fossil fuel derived precursors, formic acid can be obtained by renewable means such as the electrochemical reduction or catalytic hydrogenation of CO_2 (the energy or hydrogen used in such processes must be derived from renewable energy sources) [3–7]. DFFCs operate under alkaline conditions, which is advantageous as both the formate

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Pd-CeO2

ACS APPLIED ENERGY MATERIALS

Article

Palladium–Ceria Catalysts with Enhanced Alkaline Hydrogen Oxidation Activity for Anion Exchange Membrane Fuel Cells

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Supporting Information

ABSTRACT: Anion exchange membrane fuel cells (AEMFCs) offer several important advantages with respect to proton exchange membrane fuel cells, including the possibility of avoiding the use of platinum catalysts to help overcome the high cost of fuel cell systems. Despite such potential benefits, the slow kinetics of the hydrogen oxidation reaction (HOR) in alkaline media and limitations in performance stability (because of the degradation of the anion conducting polymer electrolyte components) have generally impeded AEMFC development. Replacing Pt with an active but more sustainable HOR catalyst is a key objective. Herein, we report the synthesis of a Pd–CeO_2/C catalyst with engineered Pd-to-CeO_2 interfacial contact. The optimized Pd–CeO_2 interfacial contact affords an increased HOR activity leading to >1.4 W cm^{-2} peak power densities in AEMFC tests. This is the only Pt-free HOR catalyst yet reported that matches state-of-the-art AEMFC power performances (>1 W cm^{-2}). Density functional theory calculations suggest that the exceptional HOR activity is attributable to a weakening of the hydrogen binding energy through the interaction of Pd atoms with the oxygen atoms of CeO_2. This interaction is facilitated by a structure that consists of oxidized Pd atoms coordinated by four CeO_2 oxygen atoms, confirmed by X-ray absorption spectroscopy.

KEYWORDS: *fuel cells, platinum free, anion exchange membrane, palladium, ceria*

1. INTRODUCTION

It is well-known that the kinetics of the hydrogen oxidation reaction (HOR) in alkaline media is much slower than in acidic solutions.[1,2] A recent comprehensive review of the current understanding of HOR electrocatalysis in basic media highlights the challenges involved in developing new materials with high activity in this medium.[3] The large overpotential for the HOR at high pH,[5] combined with the low efficiency and poor stability of anion exchange membranes (AEMs),[6−8] are the two main obstacles to the development of high-performance anion exchange membrane fuel cells (AEMFCs).[9−11]

The HOR activity of carbon-supported noble metals (Pt, Pd, and Ir) decreases by around 2 orders of magnitude when transitioning from low to high pH.[12] Only recently have researchers approached the problem in a systematic manner with the purpose of elucidating the mechanisms and defining the activity descriptors for the HOR at high pH.[2,13−18] Most importantly, the role of OH* in the HOR process under

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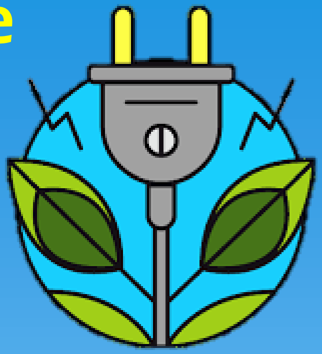
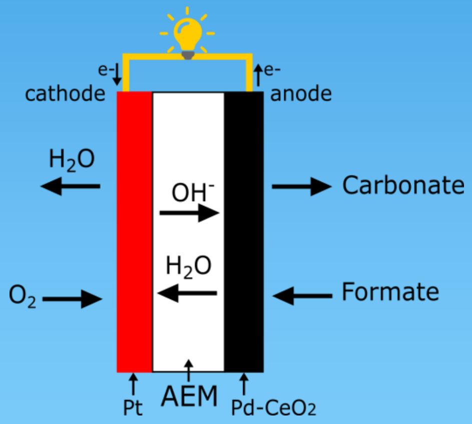
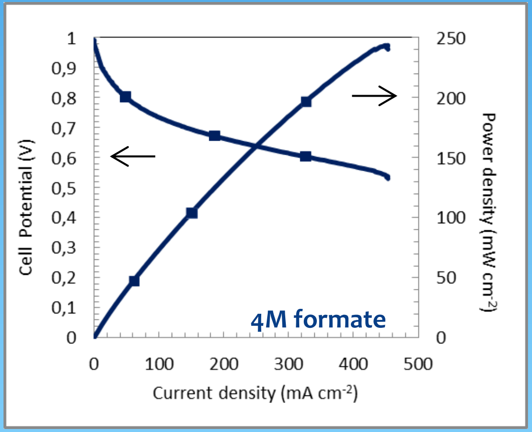
Pd-CeO2

Celle a combustibile







DFFC
(direct formate fuel cell)

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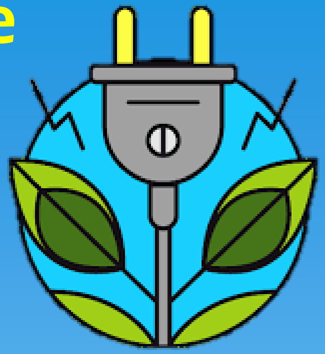
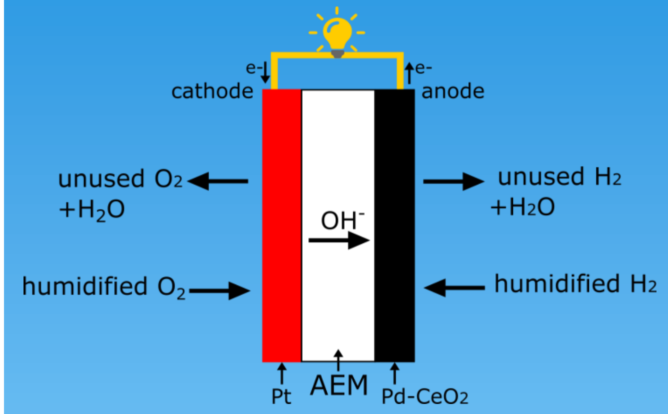
Pd-CeO2

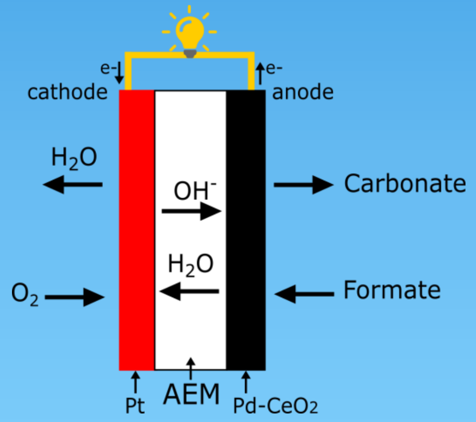
Celle a combustibile





AEMFC

(H_2/O_2 Alkaline Anion Exchange membrane fuel cells)



DFFC

(direct formate fuel cell)

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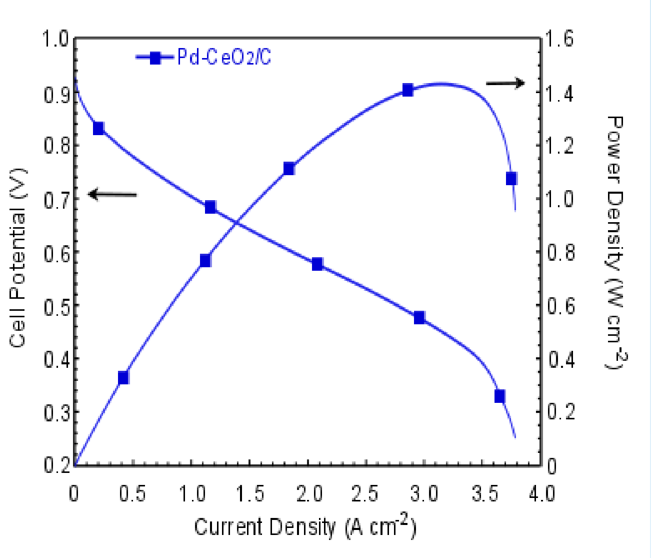
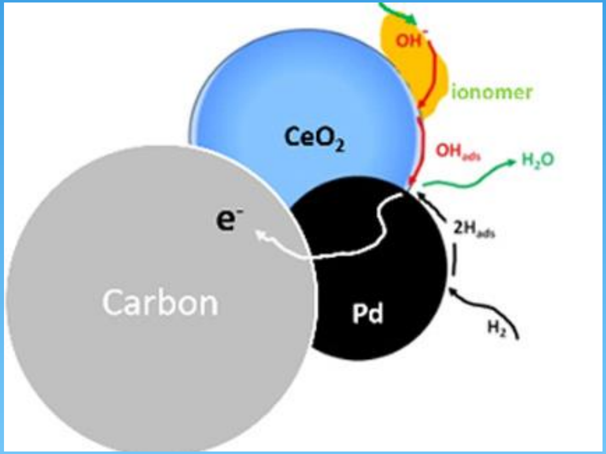


AEMFC
(H_2/O_2 Alkaline Anion Exchange membrane fuel cells)

Pd-CeO2 è il primo catalizzatore anodico Pt-free riportato in letteratura in grado di raggiungere densità di potenza > 1 W cm^{-2} in AEMFC



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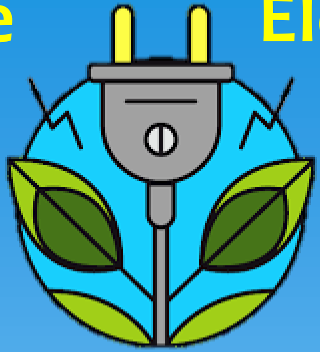
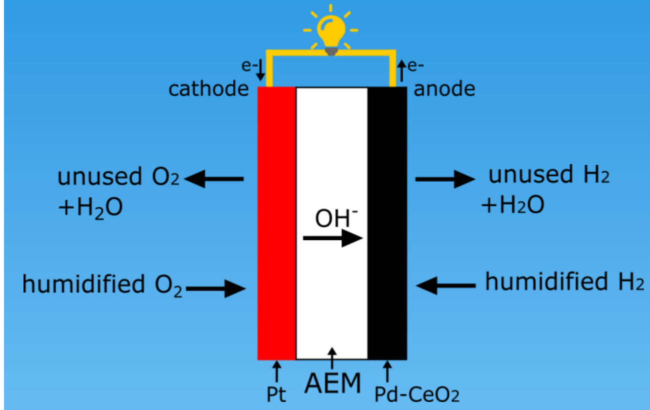
Pd-CeO_2

Celle a combustibile

Rh

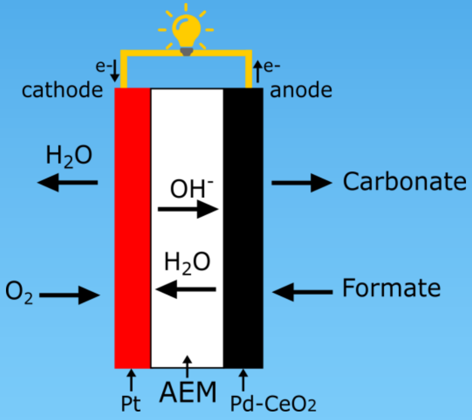
Elettrolizzatori





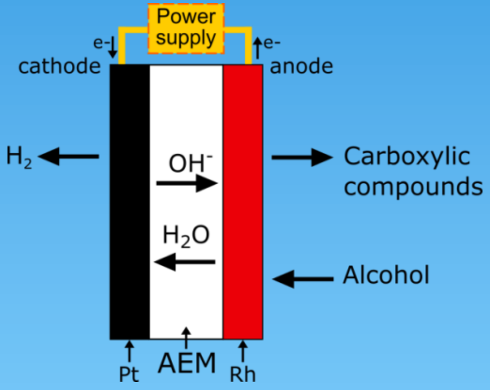
e-
e-
cathode
anode
unused O_2 +H_2O
unused H_2 +H_2O
OH^-
humidified O_2
humidified H_2
Pt
AEM
Pd-CeO_2

AEMFC
(H_2/O_2 Alkaline Anion Exchange membrane fuel cells)



e-
e-
cathode
anode
H_2O
OH^-
Carbonate
H_2O
O_2
Formate
Pt
AEM
Pd-CeO_2

DFFC
(direct formate fuel cell)



Power supply
e-
e-
cathode
anode
H_2
OH^-
Carboxylic compounds
H_2O
Alcohol
Pt
AEM
Rh

AEMAE
(Anion Exchange Membrane alcohol electrolyzers)

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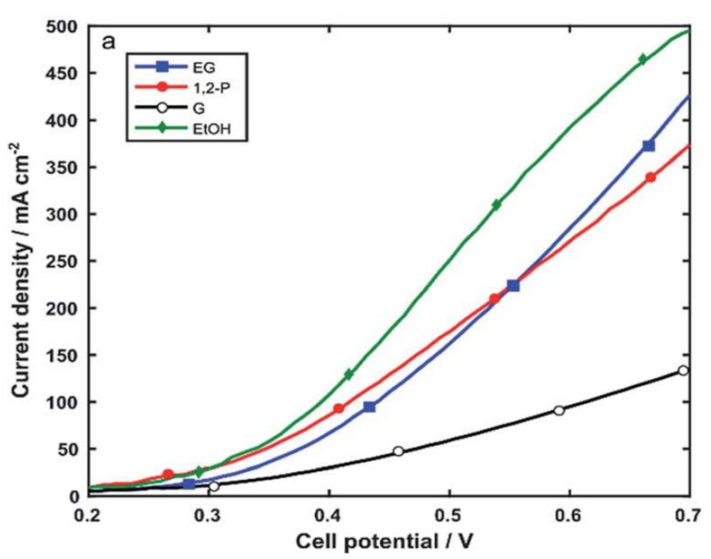
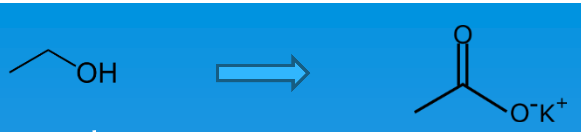


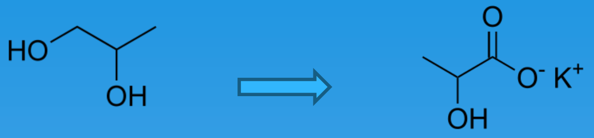
AEMAE
(Anion Exchange Membrane alcohol electrolyzers)

Consumo energetico per la produzione di idrogeno compreso tra **9-14 kWh kg^{-1}$_{H_2}$** a seconda dell'alcol usato come combustibile

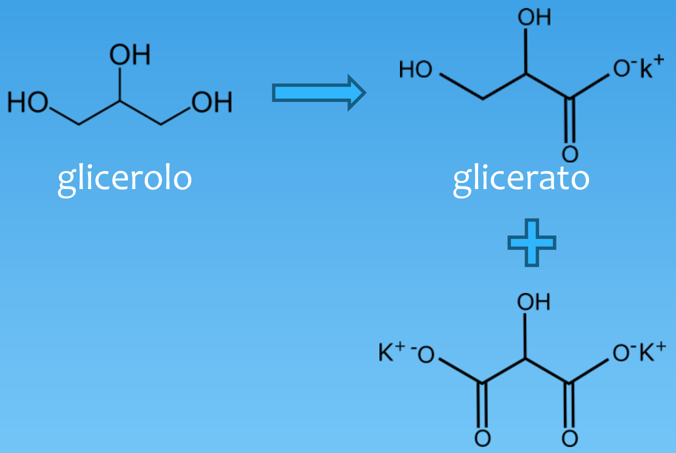
Risparmio fino a 41 kWh Kg^{-1}$_{H_2}$ rispetto agli elettrolizzatori ad acqua!!



etanolo acetato

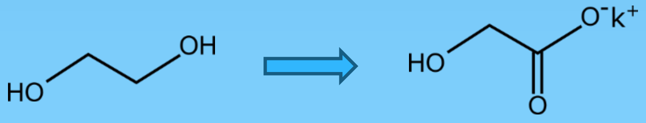


1,2-propandiolo lattato



glicerolo glicerato

tartronato



glicole etilenico glicolato

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