

Short communication

Electrodeposited PtRu on cryogel carbon–Nafion supports for DMFC anodes

C. Arbizzani, S. Beninati, E. Manferrari, F. Soavi, M. Mastragostino*

Dipartimento di Scienza dei Metalli, Elettrochimica e Tecniche Chimiche Via S. Donato 15, 40127 Bologna, Italy

Received 21 February 2006; received in revised form 28 April 2006; accepted 9 May 2006

Available online 23 June 2006

Abstract

For a high catalytic activity of the anodes in DMFC at low noble metal content a fine dispersion of PtRu on carbon supports is required and to this purpose we prepared and investigated high specific surface area cryogel carbons of controlled mesoporosity. Two carbons CC1 and CC2 with pore-size distribution centered at 6 and 20 nm were obtained by sol–gel polycondensation of resorcinol and formaldehyde, followed by a freeze-drying procedure, a versatile and low-cost method to provide after pyrolysis carbons of controlled porosity. Electrodeposited PtRu on CC2-Nafion support with ca. $100 \mu\text{g cm}^{-2}$ of Pt displayed a good catalytic activity for methanol oxidation of 85 mA mg^{-1} of Pt after 600 s at 492 mV versus NHE and 60°C in H_2SO_4 0.1 M– CH_3OH 0.5 M when the Pt-to-C mass ratio was ca. 10%. The catalytic activity tests and XRD and SEM analyses demonstrated the stability of the prepared electrodes upon catalysis in the time scale of our measurements. Strategies to further increase the catalytic activity of the PtRu/cryogel carbon–Nafion electrodes for methanol oxidation are discussed.

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Keywords: Cryogel carbon; Direct methanol fuel cell catalyst; PtRu electrodeposition

1. Introduction

Direct methanol fuel cells (DMFCs) are under study for automotive and domestic applications as well as portable power sources, and their operating temperatures require efficient electrocatalysts to minimize kinetic voltage losses and to provide high energy conversion efficiency of the fuel. Typically, DMFC electrocatalysts are based on precious metals and their high cost still remains one of the drawbacks to the wide use of these energy conversion systems.

Carbon supported PtRu is the catalyst of choice for the DMFC anode and much research is focusing on the development of high catalytic activity electrodes for methanol oxidation by pursuing new synthetic routes as well as by developing new catalyst supports [1–7]. Carbon supports should have a high electric conductivity and a high surface area with a high percentage of mesopores in the 20–40 nm region to provide a high accessible surface area to catalyst and to monomeric units of the polymer membrane and to boost the diffusion of chemical species

involved in methanol oxidation [3,7]. Thus, carbon aerogels, which are highly conducting carbon networks featuring a high surface area, high mesoporosity and a small degree of microporosity, along with the great advantage that mesopore size can be controlled by the chemical synthesis conditions, should be more suitable supports than the generally used Vulcan XC72R carbon black [4,8–12]. According to Pekala, carbon aerogels can be obtained by catalyzed, sol–gel polycondensation of resorcinol with formaldehyde, followed by supercritical drying and pyrolysis to form porous carbon networks with nanostructures that are very sensitive to synthesis and processing conditions [9]. While the supercritical drying process makes carbon aerogels quite expensive, it has been demonstrated that mesoporous carbons with narrow pore-size distribution can also be obtained by less expensive and safer procedures such as freeze drying, the corresponding carbons being called cryogel carbons [13,14].

Electrodeposition of catalyst on carbon–Nafion substrate is a promising technique for carbon-supported PtRu preparation [2,15–21], and we have already demonstrated the viability of this procedure using commercial carbons of high surface area [6,17].

On the basis of what above reported, we have pursued the strategy of developing PtRu catalyst electrodeposited on

* Corresponding author. Tel.: +39 0512 099 798; fax: +39 0512 099 365.
E-mail address: marina.mastragostino@unibo.it (M. Mastragostino).

Table 1
Resorcinol to formaldehyde (R/F), resorcinol to catalyst (R/C), and dilution factor ($D = W/(R+F+C)$) molar ratios, and pH of the initial gelation solutions for the cryogel carbons

Carbon	R/F	R/C	D	pH
CC1	0.5	200	2.5	6.4
CC2	0.5	500	5.7	6.4

mesoporous cryogel carbons. The preparation and characterization of two different cryogel carbons and the catalytic activity for methanol oxidation of PtRu electrodeposited on cryogel carbon–Nafion support are here reported and discussed.

2. Experimental

The cryogel carbons CC1 and CC2 were prepared by polycondensation of resorcinol (R, Riedel de Haen, 99.0–100.5%) and formaldehyde (F, 37% aqueous solution, Aldrich) with Na_2CO_3 (C, Riedel de Haen, >99.8%) as gelation catalyst, followed by water/*t*-butanol (Fluka, >99.7%) solvent exchange, freeze drying and pyrolysis. The R and F precursors with selected R/F and R/C molar ratios and dilution factor $D = W/(R+F+C)$ as in Table 1 were dissolved in MilliQ ultrapure water (W, Milli-Q Simplicity system, Millipore Co.). The initial pH value was 6.4 and gelation was performed at 85 °C in sealed vessels for at least 3 days. The resulting aquagels were dipped in *t*-butanol at least three times for 24 h each to exchange the aqueous solvent and the *t*-butanol was removed by freeze-drying at –40, –30, –20 and –10 °C, each temperature being held for 24 h under dynamic vacuum. The pyrolysis step, which yielded the cryogel carbons CC1 and CC2, was carried out in a furnace (ZE Muffle Furnace) at 850 °C (2 h, heating rate 10 K min^{–1}, under moderate flux of Argon, 200 cm³ min^{–1}).

Nitrogen adsorption porosimetry measurements were carried out with an ASAP 2020 system (Micromeritics); the carbon powders and carbon–Nafion composites were dried for at least 2 h at 120 °C and 10 h at 70 °C, respectively, before testing. All the analyses of the isotherms were performed according to the density functional theory (DFT) by assuming a slit-pore geometry.

Resistivity of the carbon–Nafion composites was measured via four-point technique (FPT) by a Jandel Multiheight Probe, an AMEL Model 2053 potentiostat/galvanostat and a Hewlett Packard 3478A multimeter.

The electrodes had the following design: PtRu electrodeposited on cryogel carbon–Nafion (5% solution, Aldrich) support sprayed on SuperP (ERACHEM) carbon-coated current collector (stainless steel grid AISI316L, Delker). The SuperP carbon coating, obtained by spray of a 5:1 wt.% carbon–Teflon (60% solution, Dupont) ink, improved the adhesion of the cryogel carbon–Nafion layer to the current collector, thus reduced the contact resistance. The cryogel carbon–Nafion support was prepared from ink with 2:1 wt.% carbon–Nafion ultrasonically dispersed in isopropyl alcohol (Merck, >99.7%).

The PtRu/carbon–Nafion electrodes (ca. 0.8 cm²) were prepared by electrochemical deposition from equimolar aqueous solution 20 mM of H_2PtCl_6 (Fluka, 38% Pt) and RuCl_3 (Aldrich,

99.98%). Given the hydrophobic nature of the cryogel carbons, which we prepared, before PtRu electrodeposition the electrodes were dipped 12 h in H_2SO_4 0.1 M. The electrodeposition was performed by polarizing the electrodes for 5 s at –58 mV versus NHE followed by 30 s at 742 mV versus NHE; these steps were repeated up to a total electrodeposition charge of 1.2–2.5 C cm^{–2}, corresponding to 60–125 μg cm^{–2} of Pt, as evaluated by the tin (II) chloride colorimetric method [22]; the Pt-to-carbon and Pt-to-Nafion weight ratios ranged from 8% to 12% and from 16% to 24%, respectively.

The electrocatalytic activity of the PtRu/carbon–Nafion electrodes was evaluated in H_2SO_4 0.1 M– CH_3OH 0.5 M by linear sweep voltammetries (LSV) at 5 mV s^{–1} at 25 °C and 60 °C and by chronoamperometry (CA, stirred solution) at 60 °C and at different electrode potentials with a polarization time of 600 s.

All the electrochemical measurements were carried out with a potentiostat/galvanostat Voltalab Radiometer Copenhagen PGZ 301 under argon atmosphere in a cell with separate compartments for the Pt counter electrode and a Ag/AgCl/KCl 0.04 M reference electrode; the electrode potentials are expressed in reference to a normal hydrogen electrode (NHE).

X-ray diffraction measurements (XRD) were performed with a Philips X'Pert diffractometer, a Cu Kα ($\lambda = 1.5406 \text{ \AA}$) radiation source and Ni filter by step-scanning mode (0.04° 2θ step; $4 \times 10^{-3} \text{ } 2\theta \text{ s}^{-1}$ scan rate). Scanning electron microscopy (SEM) observations were carried with a ZEISS EVO 50 instrument.

3. Results and discussion

The cryogel carbons CC1 and CC2 were prepared by modifying the synthetic routes of mesoporous aerogel carbons reported in literature [14,23]. Our preparation route mainly differs as to the drying step of the organic gels, which follows the water/organic solvent exchange. While the CO_2 supercritical drying method for aerogel material preparation prevents the collapse of the porous structure of the organic gels, we adopted the freeze-drying procedure mainly for its lower cost. The freeze-drying process, during which the solvent is frozen and removed by sublimation, obviates the formation of a vapour/liquid interphase that is responsible for the collapse of the solid network during room-temperature solvent evaporation. Since direct aquagel freeze-drying is not feasible because of the volume variation of water upon freezing, we performed as initial step the water/organic solvent exchange, which is also required for supercritical drying, using *t*-butanol as reported in the experimental part.

Given that pore-size is expected to increase with the R/C ratio and D , we selected two compositions of the precursor solution with R/C = 200 and $D = 2.5$, and R/C = 500 and $D = 5.7$, keeping the same 0.5 R/F molar ratio and pH 6.4 as in Table 1. The two syntheses yielded mesoporous cryogel carbons CC1 and CC2 of different porosity and specific surface area as shown in Fig. 1, which reports the distribution of the micropores (<2 nm), mesopores in the 2–10 nm and 10–50 nm range and the macropores (>50 nm) in the two carbons in terms of specific volume and surface area. The CC1 carbon displays a BET-specific surface of

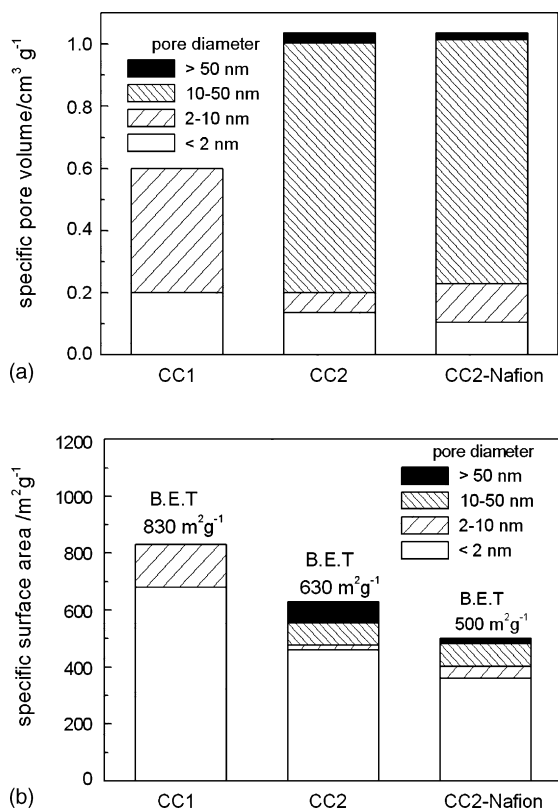


Fig. 1. Cumulative specific volume (a) and cumulative specific surface area (b) provided by micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) of the cryogel carbon powders CC1 and CC2 and of the composite CC2-Nafion.

$830 \text{ m}^2 \text{g}^{-1}$, whereas the CC2's $630 \text{ m}^2 \text{g}^{-1}$ results from a lower microporosity than that of the former carbon. CC1's mesoporosity is due to pores in the 2–10 nm range and CC2's to pores in the 10–50 nm range; Fig. 2, which shows the pore-size distribution in the 2–250 nm range in terms of incremental specific volume and surface area, indicates that CC1's pore-size is centered at 6 nm and CC2's is at 20 nm.

Given that CC1's pores are too narrow to be filled with the PtRu catalyst particles, whose PtRu crystallites are ca. 5 nm as per our electrochemical method reported above [6,17], we focused our work entirely on the carbon–Nafion support with the cryogel carbon CC2.

The porosity and electrical conductivity of the carbonaceous supports may be affected by the presence of Nafion, as well as by the procedure adopted to prepare the carbon–Nafion composite. We thus carried out porosity measurements on CC2-Nafion layers obtained by spraying the same ink used for the electrode preparation on Mylar tape; the results are reported in Figs. 1 and 2. The comparison of the data obtained for the CC2-Nafion composite with those for the CC2 carbon suggests that the Nafion binder does not obstruct the carbon's 20 nm mesopores and that its presence in the composite only decreases the micropore volume and, hence, the B.E.T. specific surface area. The measured electrical-resistivity value of the CC2-Nafion composite (prepared as for the porosimetry test) was $3.1 \pm 0.1 \Omega \text{ cm}$.

Fig. 3 reports the linear sweep voltammeteries at 5 mV s^{-1} of the PtRu/CC2-Nafion electrodes for a preliminary evalua-

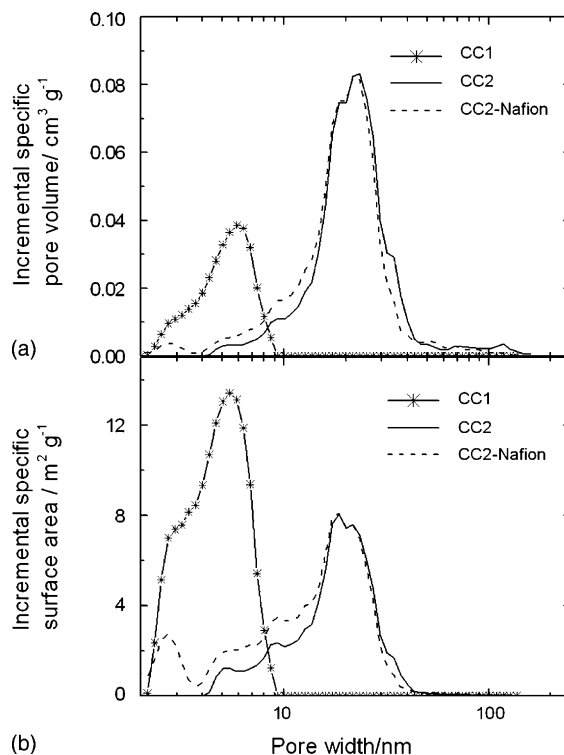


Fig. 2. Pore-size distribution in the range 2–250 nm in terms of (a) incremental specific pore volume and (b) incremental specific surface area of the cryogel carbon powders CC1 and CC2 and of the composite CC2-Nafion.

tion of the catalytic activity in H_2SO_4 0.1 M– CH_3OH 0.5 M at 25°C and 60°C . The onset of the methanol oxidation current at electrode potentials more negative than 300 mV versus NHE confirms the presence of ruthenium in the catalytic layer.

The electrocatalytic activity for methanol oxidation of the PtRu/CC2-Nafion electrodes at 60°C was tested in H_2SO_4 0.1 M– CH_3OH 0.5 M by chronoamperometry (CA) at different electrode potentials with a polarization time of 600 s so as to provide indications of the catalytic activity and the stability of the catalysts in operating conditions more representative of a working DMFC. As an example, Fig. 4 reports the CA profiles

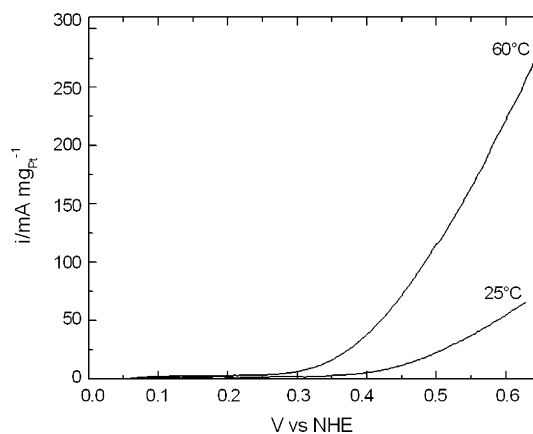


Fig. 3. Linear sweep voltammeteries at 5 mV s^{-1} in H_2SO_4 0.1 M– CH_3OH 0.5 M at 25°C and 60°C of a PtRu/CC2-Nafion electrode with $106 \mu\text{g}$ of Pt cm^{-2} and a Pt-to-CC2 weight ratio of 9.5%.

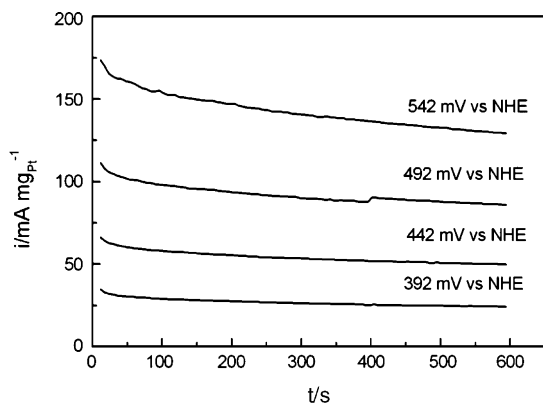


Fig. 4. Chronoamperometry profiles recorded at 542, 492, 442 and 392 mV vs. NHE in H_2SO_4 0.1 M– CH_3OH 0.5 M at 60°C of a PtRu/CC2-Nafion electrode with $106\ \mu\text{g}$ of Pt cm^{-2} and a Pt-to-CC2 weight ratio of 9.5%.

recorded at the different potentials for an electrode with $106\ \mu\text{g}$ of Pt cm^{-2} and a Pt-to-CC2 weight ratio of 9.5%. The electrode displayed a good catalytic activity with a methanol oxidation current of ca. 130, 85, 50 and 25 mA mg^{-1} of Pt after 600 s at 542, 492, 442 and 392 mV versus NHE, respectively. These are the best results for the PtRu/CC2-Nafion electrodes we prepared and the mean value of the electrocatalytic activity displayed by the electrodes with a Pt-to-carbon ratio in the range 8–12% was 110 and 15 mA mg^{-1} of Pt after 600 s at 542 and 392 mV versus NHE, respectively. As noted in Fig. 4 the electrocatalytic activity was also almost stable in the short time span of our tests.

The stability of the PtRu crystalline phase upon catalysis is confirmed by the XRD analyses on the PtRu/CC2-Nafion electrodes in the 5° – 90° 2θ range. The main (1 1 1) reflex of the PtRu centered at 40.04° 2θ , shown in Fig. 5, does not change position and width upon catalytic tests and indicates that the crystalline phase consists of a PtRu alloy with Pt:Ru ca.85:15 atomic ratio and crystallite dimension of ca. 6 nm as evaluated from Ref. [24] and by Scherrer's equation, respectively.

The morphology of the PtRu electrodeposited on CC2-Nafion was evaluated by SEM analyses, which indicated that the PtRu

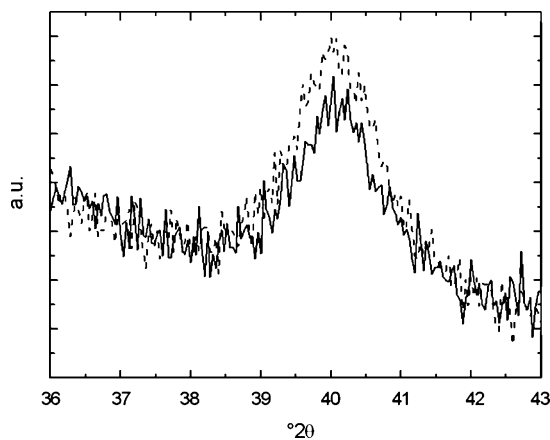


Fig. 5. (1 1 1) XRD diffraction peak of PtRu/CC2-Nafion electrodes before (solid line) and after (dashed line) the electrocatalytic tests (ca. $100\ \mu\text{g cm}^{-2}$ of Pt).

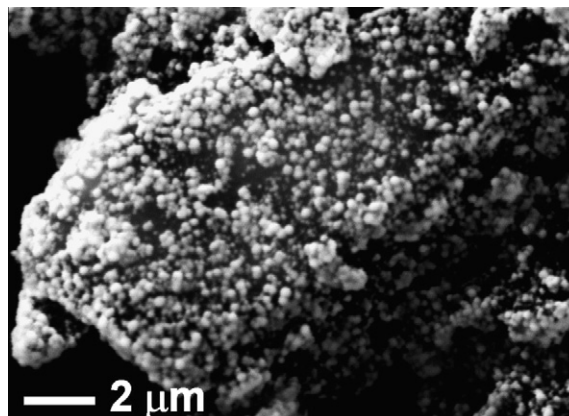


Fig. 6. SEM images of a PtRu/CC2-Nafion electrode ($106\ \mu\text{g cm}^{-2}$ of Pt).

deposits do not significantly modify in size upon catalysis. However, as shown in Fig. 6, which reports an SEM image of a PtRu/CC2-Nafion electrode after the catalytic tests, the PtRu consists of clusters of 50–200 nm, which are too wide to take advantage of the 20 nm-centered mesoporosity of the CC2-Nafion support for a high catalytic surface, and back-scattered electron images (not reported here) did not evidence smaller PtRu particles in the carbon pores. Presumably, the hydrophobic nature of the CC2 carbon, suggested by a slow, visually observed water adsorption, hinders the penetration of the PtRu aqueous precursors in its inner pores, with consequent growth and agglomeration of the catalyst on the outer surface of the carbon support. On the other hand the hydrophobic nature of the CC2 cryogel carbon is not surprising after the pyrolysis step at 850°C in Ar atmosphere. Chemical activation of cryogel carbon surface with hydrophilic moieties should improve precursor impregnation and metal nucleation in all the carbon mesopores, providing homogeneous deposition of small-size PtRu particles in the entire mesoporous carbon surface [25,26]. Given that pulsed electrochemical deposition at high current density within the ms time scale enhances nucleation vs. growth of metals [18–21], the use of this technique to deposit PtRu on activated cryogel carbons should further enhance catalyst morphology and, hence, the catalytic activity of PtRu, as well as activated cryogel carbons with mesopores wider than 20 nm should better disperse the PtRu clusters.

4. Conclusions

Cryogel carbons are good candidate supports for PtRu catalysts for methanol oxidation for their tunable mesoporosity and high surface area. The freeze-drying preparation of CC1 and CC2 is versatile and yields carbons of controlled mesoporosity, with the additional advantage of synthesis cost reduction vis à vis the methods based on supercritical drying.

The cryogel carbon CC2 displayed a pore-size distribution centered in the 20 nm value and its porosity was not significantly modified by Nafion in the CC2-Nafion composite. The intimate structure of cryogel carbons, which can be described as a carbon network, provides good electrical conductivity in the CC2-Nafion support.

PtRu electrodeposition on CC2-Nafion support is a simple and fast technique to obtain electrodes with good catalytic activity for methanol oxidation at low Pt content (ca. $100 \mu\text{g cm}^{-2}$) and good stability upon catalysis. The best performing electrode with $106 \mu\text{g}$ of Pt cm^{-2} and a Pt-to-CC2 weight ratio of 9.5% displayed, in H_2SO_4 0.1 M– CH_3OH 0.5 M at 60°C , specific methanol oxidation currents of 130 and 25 mA mg^{-1} of Pt after 600 s at 542 and 392 mV versus NHE, respectively. Note too that XRD and SEM analyses demonstrated the stability of the prepared electrodes upon catalysis, at least in the short time scale (2–3 h) of our measurements.

The SEM analyses revealed that in PtRu/CC2-Nafion electrodes the catalytic layer is made of 50–250 nm clusters which cannot fill the 20 nm mesopores of the CC2-Nafion support. PtRu aggregation on the outer surface of the carbon is presumably due to the hydrophobic nature of CC2 that hinders PtRu aqueous precursor uptake in the inner pores. Thus, work is in progress in our laboratory to prepare cryogel carbons chemically activated by hydrophilic moieties to favor carbon impregnation with precursors, as well as to develop pulsed electrochemical deposition procedures of PtRu on such activated cryogel carbons in the ms time scale. These strategies should favor PtRu nucleation inside the carbon mesopores, hence improve the metal dispersion on the carbon–Nafion support and yield PtRu catalysts of increased specific activity for methanol oxidation.

Acknowledgements

Research funded by MIUR (FISR Bando 2001) under the Italian project “Sviluppo di membrane protoniche composite e di configurazioni elettrodeiche innovative per celle a combustibile con elettrolita polimerico”.

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