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High Electrocatalytic Response of a Mechanically Enhanced NbC Nanocomposite Electrode Towards Hydrogen Evolution Reaction

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Abstract

Resistant and efficient electrocatalysts for hydrogen evolution reaction (HER) are desired to replace scarce and commercially expensive platinum electrodes. Thin film electrodes of metal-carbides are a promising alternative due to their reduced price and similar catalytic properties. However, most of the studied structures to date neglect long lasting chemical and structural stability, focusing only on electrochemical efficiency. Herein we report on a new approach to easily deposit and control the micro/nanostructure of thin film electrodes based on niobium carbide (NbC) and their electrocatalytic response. We will show that, by improving the mechanical properties of the NbC electrodes, microstructure and mechanical resilience can be obtained whilst maintaining high electro catalytic response. We also address the influence of

other parameters such as conductivity and chemical composition on the overall performance of the thin film electrodes. Finally, we show that nanocomposite NbC electrodes are promising candidates towards HER, and furthermore, that the methodology presented here is suitable to produce other transition metal carbides (TM-C) with improved catalytic and mechanical properties.

Introduction

Energy production is a high concern worldwide with great attention and funding devoted to solving our dependency on fossil fuels. In the past few years, hydrogen has been gaining attention due as an energy vector and its pollution-free and easy combustion features which make it an attractive alternative to conventional fuels^{1,2}. Although many hydrogen production mechanisms have been proposed, one of the most promising candidates is the electrochemical splitting of water³, in which the so-called hydrogen evolution reaction, (HER), provides excellent efficiency and allows the use of alternative electric sources⁴⁻⁶. Although this method yields high quantities of hydrogen, it is still a commercially unviable technology, mainly due to its dependency on high cost of platinum as efficient catalyst electrode for large scale energy applications. It is therefore of considerable importance to find efficient, stable and reliable substitute electrodes capable of being mass produced at low cost^{7,8}.

Diverse inorganic electro-catalytic substitutes for Pt have been proposed⁹ mostly based in carbon¹⁰/carbides¹¹, sulphides¹² and phosphides¹³, with the most promising results coming from molybdenum¹⁴⁻¹⁶ and tungsten¹⁷⁻¹⁹ based compounds, because of their Pt-like catalytic behaviour^{20,21} and greater availability when compared with Pt^{6,22}. Nevertheless, most of the transition metals (TMs) have shown HER capability^{23,24}, especially enhanced when presented as a TM-carbide compound²⁵⁻²⁷. In pursuit of novel, inexpensive and efficient replacements for Pt as HER electrocatalyst electrodes, many morphologies have been explored¹², ranging from 2D materials²⁸⁻³² to highly porous structures^{33,34}, all showing important improvements in the efficiency of the HER.

Typical approaches in the development of new electrodes have focused on structures which have poor mechanical resilience and concomitant poor industrial applicability. Tough electrochemical electrodes rely on high surface areas and improved catalytic centres³⁵⁻³⁷, it is important not only to optimize their catalytic response, but also to guarantee their structural integrity and mechanical

performance, which are important aspects limiting the vast majority of highly promising catalytic surfaces and composites¹¹.

Niobium Carbide (NbC) has shown several advantages over other transition metal, first of all it is both orders of magnitude cheaper and more abundant than Pt catalyst. Additionally, NbC has shown high electric conductivity and also electro catalytic towards HER³⁸, only super pass by MoC and WC^{2,38-40}. Equally important, NbC has shown excellent mechanical properties both as alloy filler and as nanocomposite structure⁴¹⁻⁴⁴.

Here we report on a new class of catalytic electrode demonstrating improved mechanical and functional properties towards HER catalysis. The electrode is a nanocomposite film with a nanocrystalline phase of NbC embedded in an amorphous carbon matrix, both of controllable microstructure. The electrodes can be easily deposited on most surfaces, including thermosensitive polymeric substrates, due to the room temperature deposition and high-energy plasma used during the sputtering deposition. The NbC electrodes, with excellent structural and catalytic properties, can be regarded as a promising alternative to known TM-C electrodes, bringing interesting insights to the future design of noble metal-free HER electrodes.

Results

Synthesis and structural characterization

Nanocomposite NbC films were prepared using previously defined strategies^{42,45} keeping thickness well in the nonmetric range (120-320 nm), Figure S1. Grazing incident X-ray diffraction (GIXRD) data (Figures 1a and S2) for all the samples clearly show two crystalline phases: cubic BCC Nb (JCPDS-ICDD 34-0370) and cubic *Fm3m* NbC (JCPDS-ICDD 38-1367), with no traces of any other crystalline phase. Chemical composition of the films was investigated by X-ray photoelectron spectroscopy (XPS) with the results presented in Table 1, (Figure S3). Composition values were extracted using the relative areas equation, $C_j = \frac{\sum(A_i/S_i)}{\sum(A_j/S_j)}$, where A represents the areas under the curve and S the sensitivity factors of the C 1s, Nb 3d and O 1s peaks. Inspection of the C 1s peak (Figure 1b), which allows for the determination of the amount of free C-C carbon, also confirmed by Raman studies (Figure S4), and C-Nb in the samples, showed that the amount of free carbon diminished with the increment of r.f power applied to the Nb target, as expected. High resolution transmission electron micrographs

(HRTEM), (Figure 1c), show the nanocrystalline structure of the electrodes, which complements the results of GIXRD, showing the nanocrystalline phases of NbC embedded in an amorphous tissue. The topography of the samples was study by atomic force microscopy (AFM) (Figure 1d, S5), and showed that the roughness of the samples remained below 1.5 nm; the structure of the films was granular while phase images showed no decomposition of the crystalline phases or segregation of the elements (Table 1).

Nanomechanical characterization of the films was carried out and showed the superior mechanical properties of the films compared to those of pure or single crystalline NbC, Nb or C films^{46–48}, Table 1. The maximum hardness of the composite films was found to be 22 GPa, a value that is ≈ 4 times greater than that of commercially available steel. The improvement of the mechanical properties is attributed to the nanocomposite structure of the films and the tunability of both grain size and the amorphous phase content by the deposition condition⁴². As electrodes, the films show excellent corrosion resistance⁴⁹ and, as observed in previous works, the increment of carbon content in the electrodes correlates with the superelastic behavior of the films after deformation, demonstrating the enhanced mechanical resilience of the films (Table 1).

Figure 1: a) Comparison of Gi-XRD diffractograms of electrode films NbC100, Nbc230 and NbC20 b) XPS C 1s spectra showing the C-C and NbC bondings for all the samples. c) SEM and HR-TEM images of NbC100 sample. d) Surface topography NbC100 and elastic recovery for pure C and NbC100samples.

Figure 2. EELS analysis of NbC100, a) L_3 onset and change across profile. b) Strain images under indentation (top) and on pristine areas (mid panel); bottom profile shows the average strain.

The existence of graphitic like C-C phases contributes to the high elastic recovery of the samples, which makes them ideal for flexible substrates⁵⁰. HR-TEM and EELS studies performed on the NbC(82%)-C-C(9%) mixture, called NbC100 hereafter, allowed the investigation of microstructural damage of the films after indentation (load vs displacement) experiments. As expected from previous HRTEM images, Figure 1c, the area under the indentation is composed

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of NbC nanocrystals around 5nm in size. Fractures of the substrate follow the (11-1) and (1-11) crystalline directions (zone axis is $[011]_{\text{Si}}$), and clearly follow the indenter's tip shape, (Figure 2b). EELS spectrum imaging (Figure 2a), shows a shift of 1 eV in the position of the Nb L3 edge due to the presence of the 20nm buffer layer. These changes are attributed to the environment change between the NbC in the film and the Nb buffer layer. A peak shift to lower energies when the Nb is more reduced has been observed in oxides^{51,52}, and, in the case of carbides, confirms the change from NbC to a metallic Nb⁰ adhesion layer. Geometrical phase analysis (GPA)⁵³ shows a lattice expansion of 5%, both in the directions parallel and perpendicular to the interface (referred as X,Y or horizontal, vertical) with respect to the relaxed silicon crystal lattice. As can be seen from the analyses in Figure 2b, this expansion is well above the noise level. The GPA results suggest a diffusion of Nb into the substrate that induces the expansion of the crystal lattice. Nevertheless, these results clearly show the superior resilience of the films to deformation and fracture.

Further characterization of the films, including electrical conductivity, was done by topographic THz examination. Measurements were performed on all the samples and showed a direct dependency of the conductivity (ρ) with chemical composition. Additionally, the topographical maps, Figure S6, allowed the calculation of the average resistivity per-sample by statistically analyzing the whole surface of the films. Conductivity was found to increase monotonically with Nb content, from 0.08 mS in pure C, to 0.6 mS in pure Nb. Table 1. We attribute the observed excellent homogeneity in conductivity to the sputtering deposition method.

Table 1: Chemical, morphological, mechanical and electrical properties of the samples, abbreviations stand for RMS (roughness mean square), *H* (hardness), *E* (Young modulus), Re (elastic recovery), ρ (mean conductivity).

Sample	Nb (r.f-W)	Nb (at.%)	C (at.%)	O (at.%)	C-C (%)	Nanocrystal Size(nm)	RMS(nm)	<i>H</i> (GPa)	<i>E</i> (GPa)	Re (%)	ρ (mS)
Pure C	0	0	99	1	99	-	0.79	12±0.3	96.6±2	81	0.08±0.02
NbC20	20	9	86	5	82	~2	0.82	13±2.3	158.3±5	69	0.15±0.01
NbC50	50	37	56	7	30	2-5	0.93	16±1.3	183.8±12	70	0.3±0.01
NbC100	100	52	39	9	9	5-8	1.20	22.5±0.5	191.7±5.7	85	0.45±0.02
NbC230	230	59	30	11	5	10-15	1.65	20.8±1.2	237.37±5.9	74	0.52±0.01
Pure Nb	230	72	10	18	0	>10	1.74	8.5±0.9	152.85±6	49	0.6±0.02

Figure 3: **a)** Polarization curves for all NbC electrodes, fast sweep $\nu = 30 \text{ mV/s}$; **b)** Stability sweeps for NbC100; **c)** Tafel plots for NbC100 and Pt electrodes.

Electrochemical characterization

The electrochemical activity of the different samples of C, NbC, Nb and bare platinum as reference are shown in Figure 3a as polarization curves registered in sulfuric acid solution without resistance (iR) compensation. The onset potential (η) for the electrochemical hydrogen electrode reaction (HER) fits the range from -0.22 to -0.85 V *vs.* the normal hydrogen electrode (NHE) for all tested materials. The bare Pt electrode exhibits the typical high efficiency behavior, with η located close to zero.

As it can be seen in Figure 3a, the onset potential of the electrode films shifts to more negative values for the pure materials such as C ($\eta = -0.75$ V) and Nb ($\eta = -0.73$ V) *vs.* NHE, indicating their lower activity (Figure S7). The partial mixtures of NbC20, NbC50 and NbC230 show low activity, with values comparable to those of pure C and Nb. Of all the fabricated materials, NbC100 exhibits a large cathodic current density with a small onset over potential of -0.22 V *vs.* NHE, beyond which the cathodic current turns to more negative potentials, with an onset potential of $\eta = -0.47$ V *vs.* NHE (Figure 3a). This value is higher compared to other NbC based electrodes⁴⁰.

In order to verify the stability of the electrochemical behavior, LV curves were registered after 200 cyclic voltammetry (CV) scans (not shown) within the cathodic regime in 0.1M H₂SO₄ as given in Figure 3b. As can be observed, subsequent LV routes did not result in any shift of the onset potential or change in current value as in the case of pure Pt. Therefore, the fabricated NbC100 sample could be regarded as a stable electrode material and a promising alternative for the expensive Pt electrode

Figure 3c shows Tafel plots for the NbC100 sample and Pt for comparison purposes. The linear parts of these plots were analyzed according to the Tafel equation ($\eta = b \log j + a$, where j is the current density and b is the Tafel slope), yielding slopes of approximately 28, and 35 mVdec⁻¹ for bare Pt and NbC100 sample, respectively. The determined Tafel slope for the platinum catalyst is close to the reported value for a commercial catalyst⁵⁴ and consistent with the known mechanism of HER on Pt. The value obtained for NbC100 is only 7 mVdec⁻¹ higher compared to Pt, and much lower than other metal carbide based electrode materials tested in acidic environment, such as MoC, (41 mVdec⁻¹)⁵⁵, Mo₂C (41 mVdec⁻¹ ⁵⁶, 54 mVdec⁻¹ ⁵⁷), MoC_x (53 mVdec⁻¹)³³. Therefore, the slope of NbC100 in acidic environment proves that in this case the discharge step (Volmer

reaction) leading to formation of H_{ads} is followed by the recombination stage (Tafel reaction): $H_{ads} + H_{ads} \rightarrow H_2$ ⁵⁸ regarded as rate-limiting. As a result the whole process is driven by the Volmer-Tafel mechanism. Since a low Tafel slope at a large exchange current is favorable for an efficient HER reaction⁵⁹, the NbC100 sample could be recognized as a superior material for the hydrogen evolution reaction.

Discussion

The experimental results show that the structural integrity of the electrodes can be controlled by their composition, which concomitantly, can be tuned by the increment of the power to the Nb target. Moreover, the electrodes clearly show a nanocomposite type coating behavior^{60–65}, with enhanced mechanical properties, especially for the NbC100 sample. An important feature of the electrodes is that their structures are highly and easily controllable in terms of their amorphous and crystalline phases, having higher crystalline sizes with the increment of Nb content, and thus lower amorphous free C-C in the films, which is a desirable parameter in order to control their conductivity (Table 1). The high energetic deposition, coupled with the lack of reactive environment in the chamber, allows for the rapid nucleation of NbC nanoparticles from the incoming Nb atoms. Additionally, the plentiful flux of carbon atoms and the high thermodynamic cost required to stabilize the well-organized crystalline phases of C=C, privilege the formation of NbC_{1-x} ^{66–68} and amorphous C-C, making this process a key aspect for the nanocomposite structure.

Figure 4: Chemical composition (C-C content) vs. polarization curves: a) conductivity; b) mechanical values.

Moreover, it has been well established that nanoparticles/nanocrystals of transition metal carbides (TM-Cs) enclosed by a thin layer of carbon produce highly active HER catalytic behavior. For example, Mo_2C -C electrodes had performance indicators of Tafel $\eta = 68 \text{ mV dec}^{-1}$ and $\approx -0.14 \text{ V}$ vs. NHE⁶⁹ and Tafel $\eta = 110\text{--}235 \text{ mV dec}^{-1}$ and $\approx -0.17 \text{ V}$ vs. NHE⁵⁵. The results showed an important increment over the reported bulk values for Mo_2C (Tafel $\eta = 333 \text{ mV dec}^{-1}$ and $\approx -0.8 \text{ V}$ vs. NHE^{6,39}), an increment that is typically attributed to several aspects^{1,8,19} such as *i*) the superior surface of the Mo_2C nanocomposites with respect to that of the solid solution, *ii*) the lower electrical resistance of composites and *iii*) their high content of free carbon. The last two aspects are crucial since both of them show a level of interdependency that might influence the

general performance of the electrodes, while the first one deals with the active centers enabling the catalytic reaction.

The THz measurement results show a direct dependency of electrical conductivity, which monotonically decreases with the increment of C-C in the electrodes Figure 4a, Table 1. Additionally, the changes in conductivity of the electrodes are directly associated to their microstructure, in which the bigger NbC grains are present in the more conductive sample, clearly showing the grain boundary influence on the overall conductivity of the samples.

It is interesting to note that neither the grain boundaries nor conductivity appear to correlate with the excellent catalytic behavior or overall electrochemical performance of the NbC100 electrode. However, the NbC100 sample does show a clear peak in hardness and Young's modulus compared to that of the other fabricated samples, which could suggest that the microscopic structure that enhances the mechanical properties of the sample also contributes to the observed HER efficiency. Therefore, it is reasonable to suggest that the nanocomposite structure is somehow involved in contributing to the catalytic enhancement of the electrodes (Figure 4b).

The nanocomposite structure of the films allows for the isolation of crystalline phases of NbC in the amorphous C-C matrix, with the phases tightly packed and interdependent on each other. This structural arrangement improves the mechanical response of the electrodes by preventing the rapid expansion of fractures, which have very short diffusion lengths and are trapped by the amorphous matrix; on the other hand, the crystalline part provides a large arrangement of monocrystalline structures ready to allocate and dissipate mechanical stress^{61,62}. Additionally, the high elastic recovery of the samples has been attributed to the graphite-like structure of the C-C carbon structure^{70,71}, which was previously studied in the literature and by our group⁴², showing the clear presence of graphitic like C-C structures with the increasing carbon content and elastic recovery. This is supported by the HRTEM-EELS measurements presented above (Figure 2), in which no changes were observed in the Nb L edge after maximum indentation.

Conclusion

In conclusion, here we have presented the unique properties of nanostructured NbC electrodes towards HER. We have shown that by controlling and optimizing the microstructure of Niobium Carbide thin film electrodes, both, their mechanical and electrochemical properties can be

enhanced. Additionally, the low temperature approach used in the deposition the thin film electrodes allow for their application on thermally sensitive substrates or surfaces, which adds to their super elastic behavior expanding on their applicability. The resulting microstructure of the thin film electrodes is that of a nanostructured coating, with C-C graphitic amorphous tissue surrounding the nanocrystalline NbC grains. The thin film electrodes presented here are mechanically superior to both bulk Pt and NbC, while showing higher electro catalytic performance than previously reported bulk and powdered NbC electrodes. Further studies, supported by numerical methods, are needed in order to clearly understand the mechanism and physical reasons behind the observed enhancement.

Finally, not only have we provided experimental evidence of the competitive applications of our NbC thin film electrodes, but also our experiments suggest that the micro/nanostructure of TM-Carbide thin film electrodes are an important feature that could allow to obtain superior electrodes towards HER in this system and in other similar carbides and nitrides.

Methods

Thin Film Electrodes Deposition

Samples were deposited on silicon (001) by means of nonreactive magnetron sputtering from two separate targets of niobium (99.95%, Demaco-Holland) and graphite (99.999%, AJA international USA). The content of Nb was regulated by switching the r.f. power applied to the target (20, 50, 100, 230 W), while the carbon target was kept at 230W. Samples were grown at room temperature (297K) using a floating potential at a partial pressure of 0.25 Pa of pure argon. As a general approach, silicon substrates were sputter-cleaned using a negative bias of 180V (25W) under 4 Pa of argon for 10 minutes, then 30 nm of pure Nb were deposited. Both procedures were carried out in order to improve adhesion of the NbC films. However, the pure carbon layer did not have the buffer layer. Thickness of the samples was set between 150-200 nm above the adhesion layer.

Structural Characterization

Composition, microstructure and crystallinity of the films were assessed by several techniques, including X-ray photoelectron spectroscopy (SAGE HE100b -SPECS) with a Mg source ($K\alpha$ 1283.6 eV). Scanning electron microscopy (SEM) (JEOL JSM-6490) was used to determine the

thickness of the samples. Phase composition was investigated by grazing incidence X-ray diffraction (GI-XRD, X'Pert PANalytical –MRD) working with Cu K α radiation (1.5406 Å) and using an incident angle of 0.4°. Nanomechanical properties of the films were investigated by means of nanoindentation (TI 950-Hysitron triboindenter) with a Berkovich diamond tip working at a maximum load of 10000 μ N. Transmission electron cross section samples were thinned to electron transparency using a focused ion beam (FEI's strata 235DB FIB/SEM dual beam) and transferred to a TEM grid using the in situ lift-out technique. TEM, HRTEM, and STEM-HAADF images of the sample were acquired in a probe-corrected JEOL ARM200 equipped with a field emission gun (FEG) source and operated at 200kV. EELS measurements were performed in the same microscope using Gatan's Quantum GIF EELS spectrometer. The geometric phase analysis (GPA) was carried out using the GPA plugin by HREM Research Inc. Cross sections of the indents were prepared following the same approach reported by S.J. Lloyd et al.⁷², in which a series of indents are performed in a single row and framed by very deep indents, while the indents of interest are placed in the middle of the pattern, keeping a safe distance of 5 μ m from each other. Conductivity (ρ) and conductivity maps of the thin films were obtained using terahertz radiation (das Nano Onyx thin film inspector) from 0.3 to 30 THz, (1 mm to 10 μ m), with a pixel resolution of 1 pixel/mm². Samples were measured in reflection mode at room temperature ($\approx$ 298K).

Electrochemical characterization

The electrochemical characterization was performed with a Gamry PCI4 potentiostat-galvanostat controlled by the Gamry Instruments Framework software and AutoLab PGStat 302N system operating under the Nova software. All measurements were carried out in a standard three-electrode assembly at room temperature. 0.1 M H₂SO₄ was used as electrolyte and was purged with argon for 50 min before the electrochemical tests; an Ar cushion was kept above the electrolyte during measurements. Ag/AgCl_(NaCl sat) or Ag/AgCl/3M KCl were used as reference electrodes (REF); potentials were properly recalculated against the NHE. A platinum wire was used as counter electrode (CE) and Si plates covered by different NbC coatings or pure carbon were used as working electrodes (WE). Comparisons were made with pure Pt. The linear voltammetry curves (LV) were obtained with fast and slow scanning rates at 30 and 2 mV/s, respectively. In order to verify sample stability, the multi-cyclic voltammetry (CV) scans (not

shown) were registered in the range from -0.5 to 0 V vs. NHE. Before this test and after 200 repetitive CV scans with $v = 20$ mV/s, subsequent LV curves were measured and presented. The values of registered currents were recalculated to the current densities taking into account the geometric surface area of electrode materials.

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