



Hydrogen evolution activity and electrochemical stability of selected transition metal carbides in concentrated phosphoric acid



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ABSTRACT

Alternative catalysts based on carbides of Group 5 (niobium and tantalum) and 6 (chromium, molybdenum and tungsten) metals were prepared as films on the metallic substrates. The electrochemical activities of these carbide electrodes towards the hydrogen evolution reaction (HER) in concentrated phosphoric acid were investigated in a temperature range from 80 to 170 °C. A significant dependence of the activities on temperature was observed for all five carbide samples. Through the entire temperature range Group 6 metal carbides showed higher activity than that of the Group 5 metal carbides, attributable to the different electronic structures. Tungsten carbide among the studied electrode samples exhibited the highest HER activity. Upon anodic potential scans in the presence of oxygen, chromium, tantalum and tungsten carbides displayed passivation due to the formation of stable surface layers whereas niobium and molybdenum carbides seemed to undergo corrosion.

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1. Introduction

An important issue in the field of renewable energy technologies is effective energy storage over time [1], with different competing technological scenarios under consideration. Hydrogen, in its role as energy carrier for electrochemical energy conversion technologies such as fuel cells and electrolyzers, is proposed as a reliable, secure and clean option in association with renewable energy sources. Particularly, water electrolysis in proton exchange membrane (PEM) cells provides a favorable and practical means for hydrogen production using surplus electric energy. A significant challenge for the widespread use of water electrolysis for hydrogen production is the economic costs of this technology, related in part to the high price and scarce availability of Pt and related noble metals (such as Ir), which are the state of the art catalyst materials for PEM electrolyzers.

There is intensive research towards the investigation and development of highly active and cost-effective catalysts for electrolysis [2–4]. Group 6 transition metal carbides, among others, have been known for years for their catalytic properties, similar to those of noble metals [5–8] and explored for chemical [9] and electrochemical [10] applications.

The electrochemistry of WC in acidic aqueous media has been studied by many authors. Early work [11,12] was made to study the activity of the material for hydrogen oxidation in sulfuric acid as well as the adsorption of hydrogen. Some work was also done regarding the behavior in hot phosphoric acid [13]. The research in sulfuric acid media has shown that the activity of WC itself as electrocatalyst for the hydrogen oxidation reaction (HOR) showed significant activity, although lower than that of Pt [14].

Alternatively, carbides have been proposed to be used as a support for noble metal catalysts. For example, WC-supported Pt catalysts exhibit a synergistic effect with Pt for HOR [15,16]. In this regard, an interesting finding was the good resistance of WC supports and the corresponding supported catalysts towards CO poisoning [17], which is a key issue for the use of reformat hydrogen as fuel for both low and high temperature PEM cells.

In connection with this, recent efforts were made to use metal carbides as supports in catalysts for methanol oxidation [18–24]. The CO poisoning resistance is also relevant, with the carbide playing an analogous role to that of Ru in methanol oxidation reaction. In addition to Pt, WC-supported PdCo alloy nanoparticles were recently studied for formic acid electrooxidation [25].

The oxidative stability of metal carbides is of critical concern, as the oxidation occurs at potentials below the onset for the oxygen reduction reaction (ORR). Nevertheless, it has been tested as support for Pt in ORR electrodes [26–29], where the presence of Pt seems to improve the corrosion resistance of the carbide [30]. Moreover, other metals like Ag [31] and Au-Pd [32] catalysts have also been investigated with carbides as the support.

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Relatively limited work has been done to evaluate the catalytic activity of metal carbides towards the hydrogen evolution reaction (HER). Using tungsten carbides as supports for platinum catalysts Ham et al. [33] and Hsu et al. [34] reported enhanced HER activity. In addition to tungsten carbides, a few other Group 6 metal carbides have been investigated. Molybdenum carbides seem to behave in a similar way as tungsten carbides as catalyst supports [35–37], while chromium carbides show significant hydrogen evolution activity in sulfuric acid [38]. In the case of Group 5 carbides, only limited research has been done with e.g. TaC as support for IrO₂ in oxygen evolution electrodes [39].

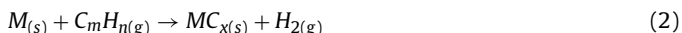
Most of these studies were carried out in the lower temperature range. Recent development of PEM technologies is aimed at operation at elevated temperatures, above 100 °C, for example, based on phosphoric acid doped polybenzimidazole membranes [40] and phosphoric acid doped perfluorinated sulfonic acid membranes for steam electrolyzers [41–43]. Significant efforts in the field are being made to explore solid acids e.g. CsH₂PO₄ as electrolytes for intermediate temperature fuel cells [44]. A better chance might exist for using metal carbides as catalysts in this temperature range [45]. In both doped membranes and inorganic solid acids, phosphoric acids and phosphates function as the proton conducting electrolyte. The electrochemical behavior of metal carbides in these media, as demonstrated recently [46], shows an important temperature dependency.

In the present work, the basic electrochemical behaviour of selected transition metal carbide surfaces in hot phosphoric acid were studied, focusing on their electrocatalytic properties towards the hydrogen evolution reaction, as well as their electrochemical stability in oxidizing conditions.

2. Experimental

2.1. Electrode preparation

In order to obtain samples with controlled electrode area, films of five metal carbides were prepared by using the parent metals as substrates. Bulk carbide materials are not easy to prepare. In general, the insertion of carbon in the metal structure requires the diffusion of carbon atoms from a carbon-containing precursor, such as graphite or a hydrocarbon:



This diffusion seems to have a high activation energy, and so all known synthesis processes for metal carbide preparation require high temperatures, as high as 1230 °C. For instance, in the case of tungsten carbides, the solid-solid W-C reaction [47] synthesis needs above 1200 °C to produce α -WC. In this case, there is the added difficulty of controlling the amount of reactants to have the right stoichiometric amount, lest significant amounts of non-desired products are obtained.

In the case of carburization with carbon-containing gases, the temperatures required are in general lower than for the solid-solid cases, in the order of 750 °C and above. Another advantage over the solid-solid synthesis is that generally better defined compositions are obtained, which is convenient for good reproducibility in the synthesis and characterisation of these materials. This class of synthesis is usually named the temperature programmed reduction (TPRe) method in the literature [48–51].

In the present work, plates of Cr, Nb, Mo, Ta and W (Goodfellow Cambridge Ltd.) were mechanically polished with SiC sandpaper (down to 4 μ m particle size) and cleaned with NaOH solution in order to remove grease and oxide impurities, and dried at 80 °C in air. The plates were carburized with 20% vol. CH₄ in H₂, through the

Table 1

Carburization temperature, obtained experimental kinetic parameters at 170 °C and activation energy for HER on carburized metals.

Metal	T _{synthesis}	log(j ₀)	m _{Tafel}	j _{-100 mV}	E _a
	°C	A/cm ²	mV	μ A/cm ²	kJ/mol
Cr	800	-4.81	76	318	73
Mo	750	-4.61	67	763	71
W	880	-4.41	56	2380	38.7
Nb	900	-5.52	135	16.6	119
Ta	950	-6.44	93	4.27	28.6

TPRe process as described elsewhere [52–55]. In a typical carburization, a W plate was placed in a quartz oven under 300 mL/min CH₄/H₂ flow for 30 min at room temperature. A temperature ramp of 8 °C/min was then applied up to 880 °C; the final temperature was held for 1 h. Other carbides were synthesized similarly, albeit at different final temperatures, as listed in Table 1. After this, the carburized plate was allowed to cool down to room temperature and stored.

2.2. Characterization

Reflexion X-ray diffraction (XRD) was used on the carburized plates. A Bruker D8 Advance diffractometer (Cu K α , 1.54056 Å) was used to detect the obtained carbide phases. The surface morphology of the samples was investigated with a scanning electron microscope (Carl Zeiss EVO MA10).

The electrochemical measurements were performed in a custom-made borosilicate glass cell (Fig. 2). The electrolyte used was 100% H₃PO₄, prepared by evaporation of 85% H₃PO₄ (Sigma-Aldrich) at 180 °C to the density (25 °C) of 1.88 g/mL. It is well known that, in the temperature range of the present study, the water vapor pressure over concentrated phosphoric acid is quite significant. In this setup, a water-cooled condenser was attached to the cell in order to minimize water losses, allowing measurements up to 170 °C. A reversible hydrogen electrode (RHE) was used as the reference electrode and a Pt disk as the counter electrode. The temperature in the cell was controlled with a hot plate within ± 1 °C. The electrolyte was purged with either pure H₂ or O₂ throughout the measurements.

HER activity measurements were performed in H₂-saturated H₃PO₄. Linear scan voltammetry at a scan rate of 1 mV/s was used

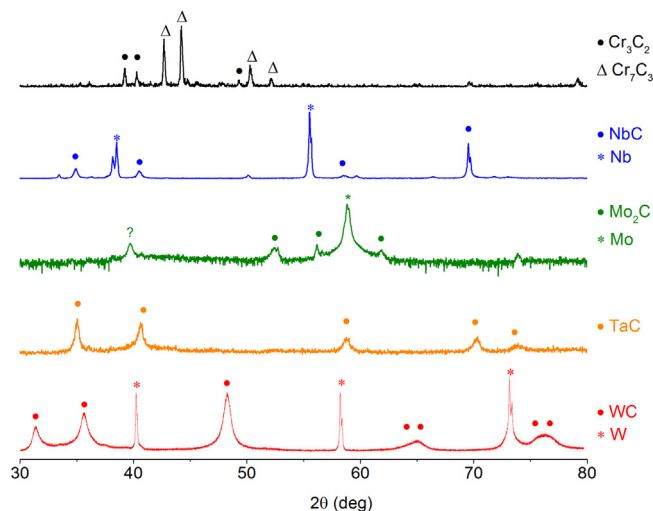


Fig. 1. XRD spectra of carburized metal plates.

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