

OXYGEN ELECTROREDUCTION ON NANOPOROUS CARBONS: TEXTURAL FEATURES VS NITROGEN AND BORON CATALYTIC CENTERS

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Introduction

Platinum-decorated carbon are considered the most efficient catalysts for oxygen reduction reaction, ORR, with a high number of electron transfer and a high positive value of overpotential¹. However, their high cost, poor durability and them being easily poisoned, prompted a need for new non-noble metal or non-metal electrocatalyst replacements. To this intent, heteroatom-doped carbon materials have attracted recent attention and among them, the performance of N and B has been explored and found promising for ORR². On these materials, reduction of oxygen occurs with a number of electron transfer close to 4. The role of pores and especially strong oxygen adsorption in the nanospace as an additional ORR mechanism has also been recently reported³. On porous carbons practically free of N and S the electron transfer number was close to 4. The results suggested that small pores of hydrophobic nature withdraw oxygen from the electrolyte and the strong adsorption in these pores promotes oxygen bond splitting and electron transfer. Other experimental and theoretical studies found that intrinsic defects in the carbon matrix, contribute to the observed enhanced ORR activity, irrespective of the presence of nitrogen⁴. Following these findings, we have investigated the influence of porosity on ORR taking place on the surface of porous carbon materials with high contents of B and N, as well as on the same highly porous carbons but with only traces of N, in order to unravel the role of small pores with strong adsorption forces and to rank their influence on ORR in comparison with that of "traditional" heteroatom-containing catalytic centers.

Materials and Methods

Carbons were synthesized from polymers heated to 1000°C (10°C/min) in a N₂ atmosphere containing 0.5% NH₃ for 3h. Boron-doped carbon were synthesized in the same condition, using a mixture polymer/boric acid with a ratio 9:1. All samples were washed in a Soxhlet apparatus. CPSS refers to the sample obtained from poly(sodium 4-styrenesulfonate) and CPSM to the one from poly(4-styrenesulfonic acid-co-maleic acid) sodium salt. CPSS-B and CPSM-B refer to the samples synthesized in the presence of boric acid. In the case of CPSS-B the carbons were washed for 7 and 4 days and they are referred to as CPSS-B1 and CPSS-B2, respectively. The textural, morphological and chemical properties of the samples were investigated by N₂ adsorption isotherms at -196°C, Raman spectroscopy, XRD, SEM, TEM-EDS, XPS and titration. The electrochemical measurements were done using a rotating ring-disk electrode in a three-electrode cell setup, with 0.1 M KOH electrolytes purged with O₂ or N₂.

Results and Discussion

Porous carbons with heterogeneous and hierarchical pore structure and a low degree of

microporosity, and containing or not B and N heteroatom (~ 10 at.% each) were synthesized. The volume of micropores and ultramicropores (<0.7 nm) is the highest for CPSM and the lowest for CPSS. Addition of boric acid increased the surface area and porosity for the CPSS series, while for CPSM it led to a decrease in these values. It also resulted, for both CPSS and CPSM, in a slight decrease in the level of defects. Longer washing time for the CPSS-B series increased the porosity, especially the ultramicroporosity, but led to lower B and N contents.

Table 1. N and B content, pore parameters, number of electron transfer (n) and ORR onset potential

| Sample | N at.% | B at.% | S _{BET} (m ² /g) | V _{tot} (cm ³ /g) | V _μ (cm ³ /g) | V _{<0.7nm} (cm ³ /g) | n | Onset (mV) |
|---------|--------|--------|--------------------------------------|---------------------------------------|-------------------------------------|---|------|------------|
| CPSS | 1.1 | 0 | 389 | 0.32 | 0.17 | 0.01 | 3.6 | 754 |
| CPSS-B1 | 7.2 | 7.2 | 600 | 0.46 | 0.24 | 0.12 | 3.94 | 827 |
| CPSS-B2 | 11.0 | 10.9 | 498 | 0.39 | 0.19 | 0.08 | 3.75 | 807 |
| CPSM | 0.8 | 0 | 1560 | 1.29 | 0.56 | 0.15 | 3.9 | 782 |
| CPSM-B | 10.2 | 8.9 | 712 | 0.89 | 0.27 | 0.10 | 3.9 | 803 |

The carbons were found to be efficient ORR catalysts, with number of electron transfer close to 4 and onset potential reaching 827 mV (on Pt/C 888 mV). However, the good performance was not exclusively found for

the carbons with high contents of boron and nitrogen, where it could be directly linked to the heteroatom-related catalytic centers. CPSM, which has the highest volume of ultramicropores, also exhibited a very good performance despite containing only traces of N and no B. The numbers of electron transfer for CPSM and CPSM-B were the same owing to the compensated effect of the decreased porosity by the heteroatom-based catalytic centers. The onset potential was higher for CPSM-B than for CPSM, which could indicate a higher effect of the heteroatoms on the onset potential than that of the porosity. However, the comparison of CPSS-B1 and CPSS-B2 showed that despite smaller amounts of boron and nitrogen, the onset potential for CPSS-B1 is the most positive one, indicating the importance of porosity in governing the extent of this parameter.

Conclusions

By adjusting the porosity of carbons it is possible to derive metal and heteroatom free ORR catalysts of an excellent performance, as that of CPSM carbon studied here. Abundant ultramicropores in carbons enhance ORR via providing strong adsorption forces. On carbons with moderate volume of ultramicropores, N and B catalytic centers compensate the porosity effect enhancing the performance. Combining both, specific porosity and B/N doping can lead to exceptional performance in ORR, as that of CPSS-B1 or CPSM-B porous carbons that have high number of electron transfer close to 4, high onset potential and high kinetic current.

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