

## **Supporting Information**

### **Oxygen reduction and methanol oxidation behaviour of SiC based Pt nanocatalysts for proton exchange membrane fuel cells**

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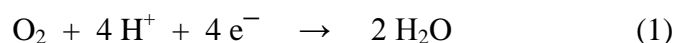
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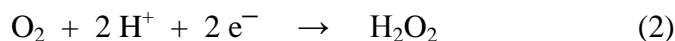
## Oxygen reduction reaction

The oxygen reduction reactions (ORR) engaged in the fuel cell activity are mass transport limited. The oxygen reduction is a multi-electron reaction and it may follow several complex mechanisms and has many elementary steps. There are two electrochemical pathways which are agreed upon to take place in the ORR. The pathway can follow either the one step 4-electron pathway (1) or the two step 2-electron pathway (2), which is also known as the peroxide pathway. These are shown below.

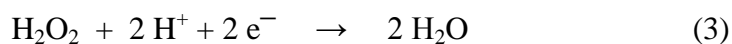
The direct 4-electron pathway:



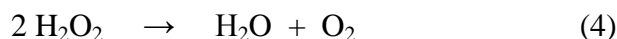
The 2-electron (peroxide) pathway:



The formed peroxide can be electrochemically reduced by another 2-electron reduction,



Or chemically decompose,



Peroxide formation is generally undesirable in the PEMFCs since they will then also contain the highly aggressive radicals  $\text{HO}\cdot$  and  $\text{HO}_2\cdot$ , which may lead to the degradation of vital components.

## Instruments used

The Pt/SiC samples were characterized by X-ray diffraction (XRD), using a Siemens Diffractometer D5000, and imaged in a Hitachi S-4800 scanning electron microscope (SEM). The morphology, structure, defects, and crystal phases of individual SiC nanocrystals were examined by transmission electron microscopy (TEM) using a Philips CM20 instrument operated at 200kV. The confirmation of the silicon carbide character is also done by X-ray photoelectron spectroscopy (XPS) using a SPECS PHOIBOS 100 system<sup>®</sup>. The electrochemical CV measurements were performed using a Zahner IM6eX electrochemical workstation (Zahner-Electric GmbH & Co. KG, Germany) controlled by a Thales 1.48. The RDE setup used is from Pine Research Instruments and it consists of an AFMSRXE modulated speed rotator and a tip.

## XPS Analysis

The XPS survey spectrum of Pt/SiC-SMS is shown in Fig. S1(a), while the XPS analyses of other SiC based catalysts have already been discussed in our previous publication. The XPS analysis of Pt/SiC-SMS is similar to the other two samples reported previously. The survey spectrum (resolution of 2.5 eV) is recorded for kinetic energies from 200 to 1260 eV, and is excited with an Mg X-ray source (Mg  $K_{\alpha}$ ). The XPS data have been analysed using the CasaXPS<sup>TM</sup> software. The spectra show the presence of silicon, carbon, oxygen and platinum with a relative elemental composition of 37.7, 26.8, 10.5 and 25% respectively. The amount of Pt in Pt/SiC-SMS (25%) is higher than for Pt/SiC-NS (16.4%) and Pt/SiC-SPR (20.1%); this could be due to the difference in the morphology of substrates. SiC-NS and SiC-SPR are nanocrystals of 25-35 nm and 50-150 nm respectively, while SiC-SMS have dimensions in the range of 1 – 10  $\mu\text{m}$ . The dense structure of SiC-SMS force most of the Pt to remain on the surface in contrast to the nanoporous SiC, thus showing a higher amount of Pt in SiC-SMS in comparison to Pt/SiC-NS and Pt/SiC-SPR. Pt nanoparticles may hide inside the nanopores of nanoporous SiC and may not show up in the surface sensitive XPS.

The deconvolution of C 1s and Pt 4f peaks in high resolution spectra (resolution of 1.3 eV) has been done by fitting these with pure Gaussian peaks on a linear background (shown in Fig. S1(b) & (c)). Table S2 gives the relative amount of the different components after deconvolution of C 1s and Pt 4f peaks of Pt/SiC-SMS. The deconvolution of the C 1s spectrum shows three components due to SiC, C-C and C-OH and/or C-N bonds. The Pt 4f peak is a doublet due to spin orbit splitting and it consists of 4f (7/2) at around 71.1 eV and 4f (5/2) at around 74.4 eV. Deconvolution of the Pt 4f peaks results in three doublets marked Pt(0), Pt(II) and Pt(IV) in Table S1. The most intense peak at 71.1 (4f (7/2)) can be attributed to metallic Pt, while the less intense peaks can be ascribed to +2-valent and +4-valent Pt as in PtO and PtO<sub>2</sub>.

**Table S1.** Peak deconvolution of Si 2p and C 1s regions of SiC nanocrystals based on Fig. S1.

Sample name	Peak regions	Bond type	Position	Relative %
Pt/SiC-SMS	C 1s	SiC	283.1	84.5
		C-C	285.3	5.4
		C-OH, C-N	286.8	10.1
	Pt 4f	Pt(0) I (7/2)	71.1	42.0
		Pt(0) II (5/2)	74.5	41.3
		Pt(2) I (7/2)	72.5	5.0
		Pt(2) II (5/2)	76.6	5.1
		Pt(4) I (7/2)	73.9	2.6
		Pt (4) II (5/2)	78.3	4.1

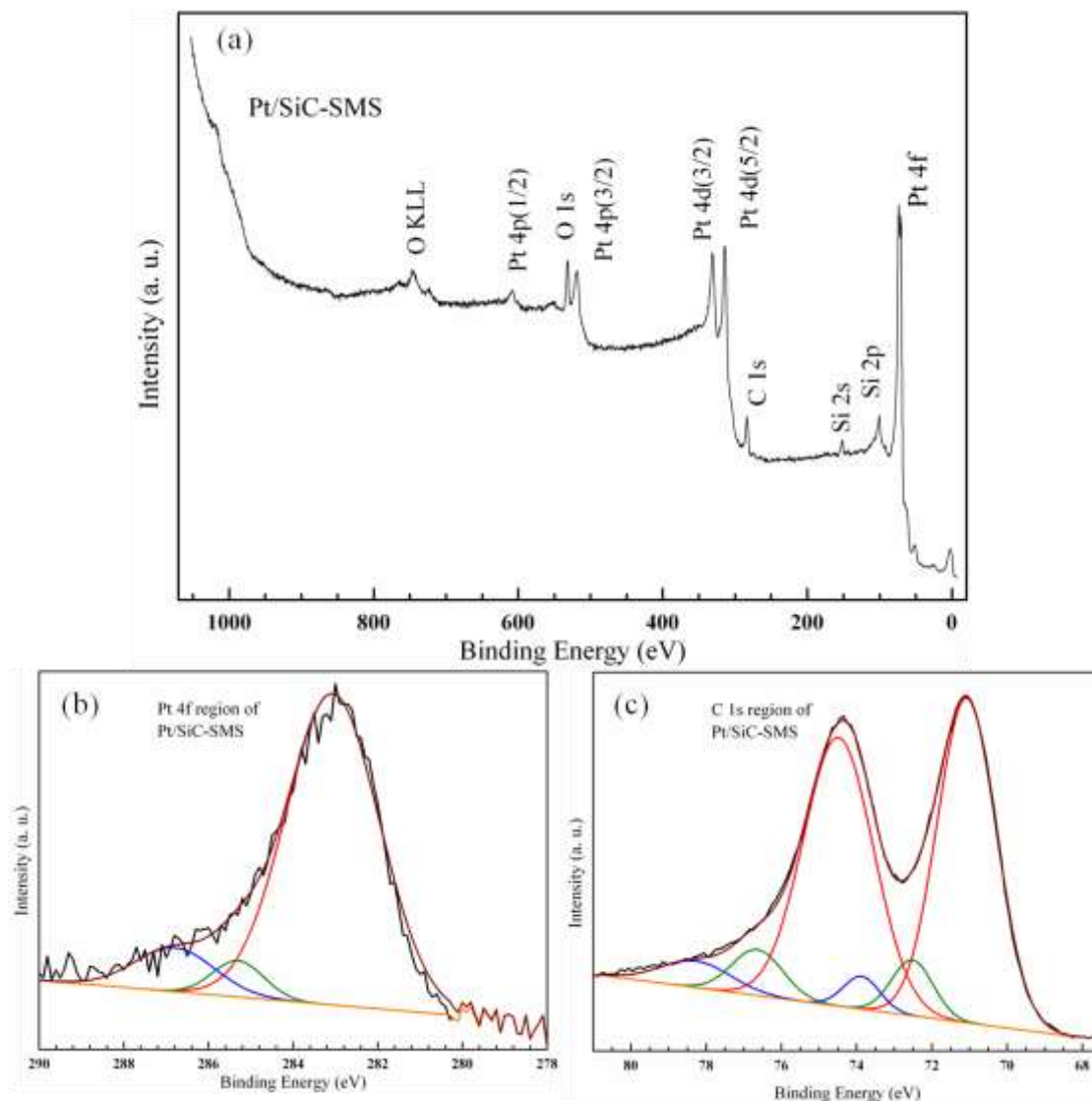


Fig. S1. The XPS survey spectrum (a) and deconvoluted C 1s (b) and Pt 4f (c) peaks of Pt/SiC-SMS.

## Pt particle size distribution

Fig. S2 shows the Pt particle size distribution of Pt/SiC catalysts. The particle sizes have been calculated from TEM images. The distributions have been fitted to Gaussians and it gives an average Pt diameter of  $3.9 \pm 2.5$ ,  $5.5 \pm 2.6$  and  $7.0 \pm 2.0$  nm for SiC-NS, SiC-SMS and SiC-SPR respectively.

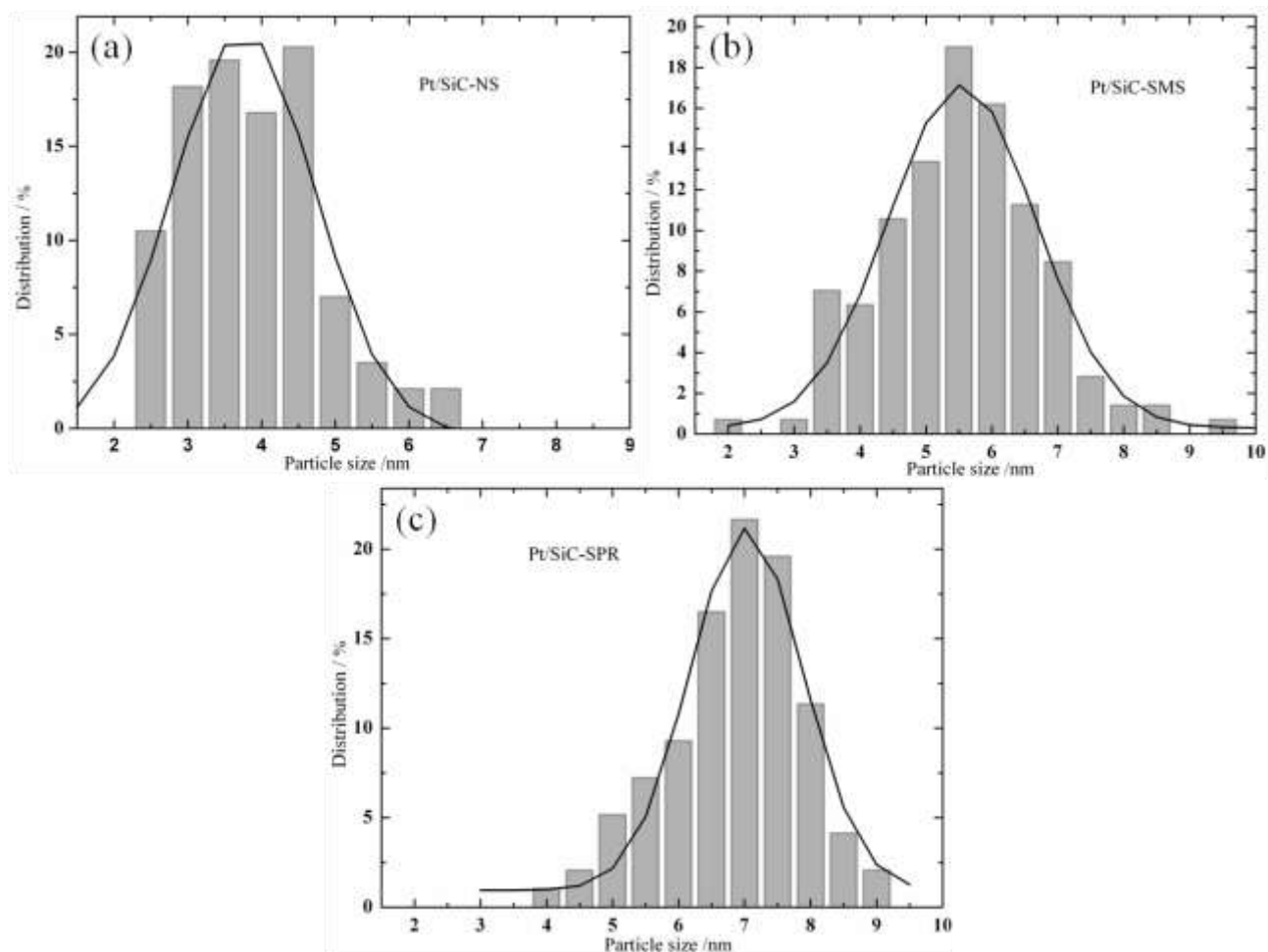


Fig. S2. Pt particle size distribution of the different catalysts (a) Pt/SiC-NS, (b) Pt/SiC-SMS and (c) Pt/SiC-SPR.

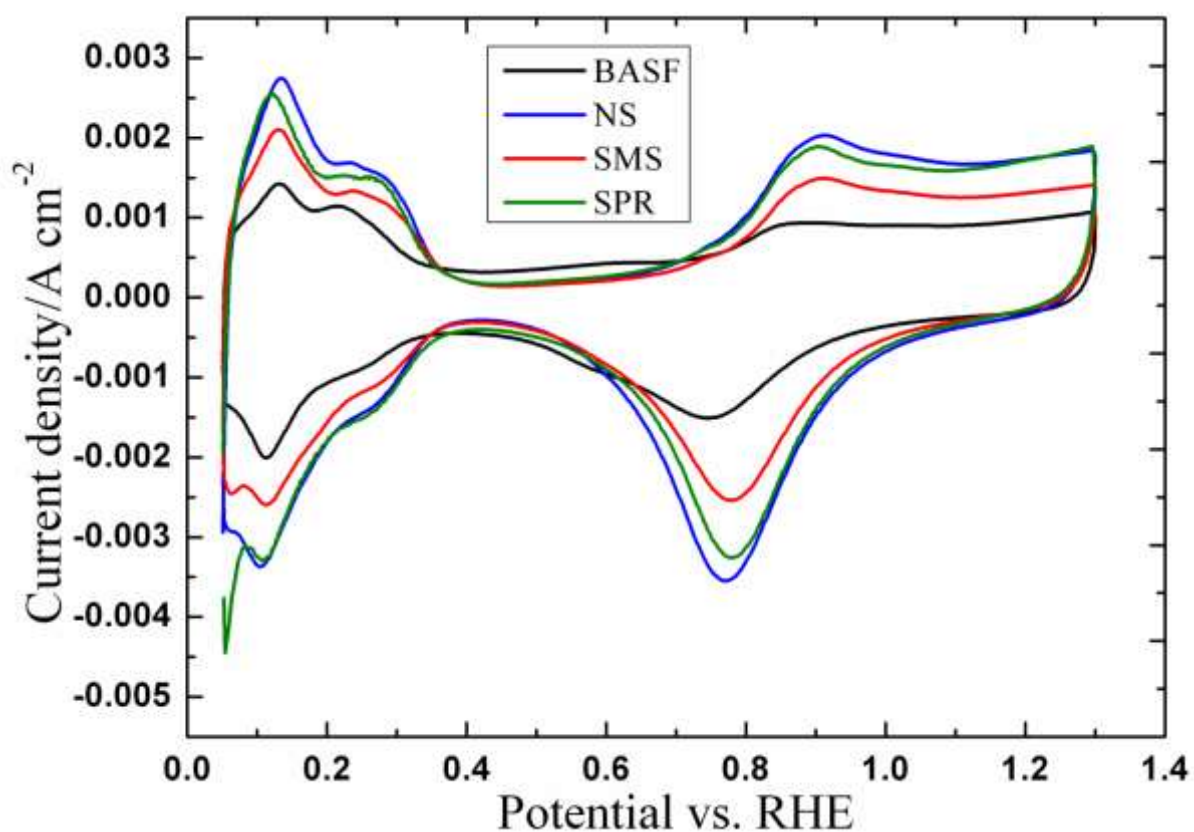


Fig. S3. Cyclic voltammograms of BASF, Pt/SiC-NS, Pt/SiC-SMS, Pt/SiC-SPR.

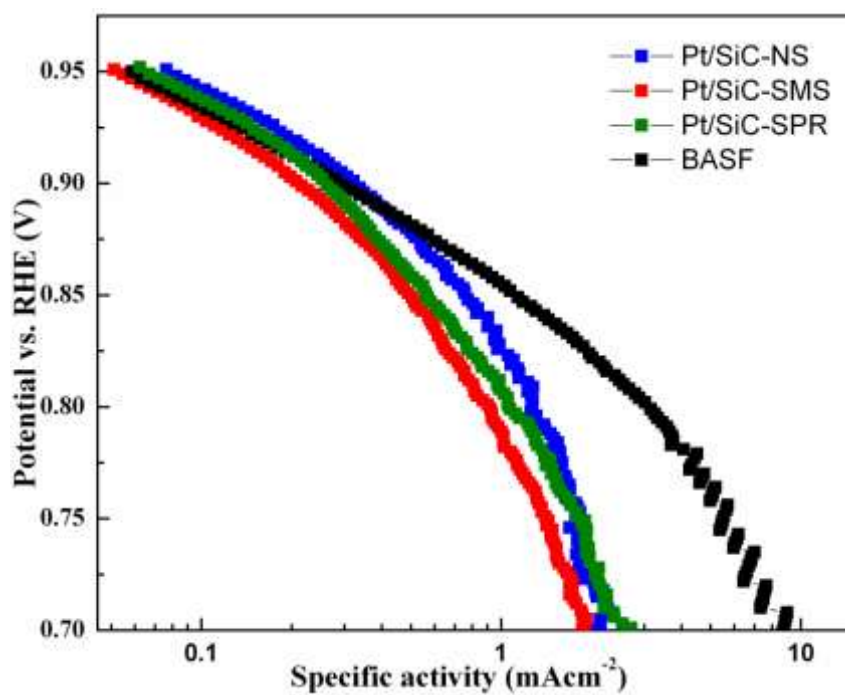


Fig. S4. Tafel plots at 1600 rpm.