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## Carbon nanotubes and other nanostructures as support material for nanoparticulate noble-metal catalysts in fuel cells

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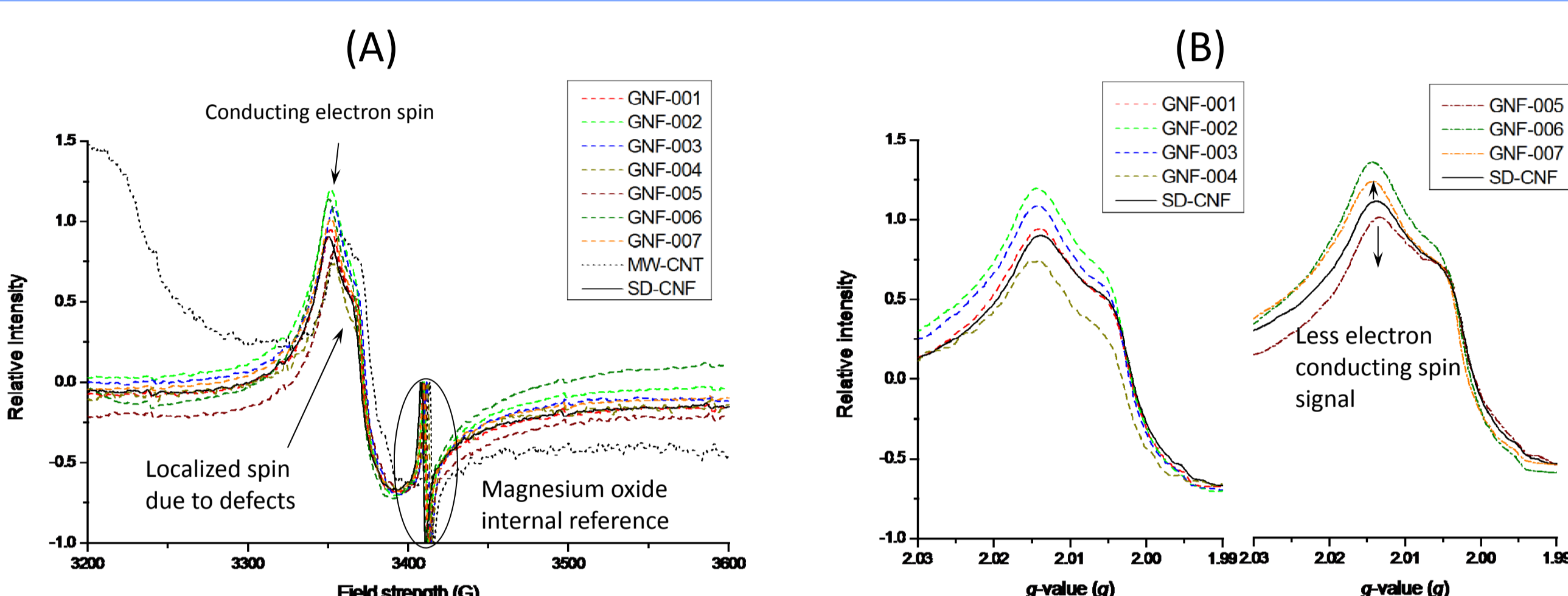
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For polymer electrolyte membrane fuel cells (PEMFC) using hydrogen as fuel and operating at low temperature (60-80°C) the most efficient catalysts for the hydrogen oxidation reaction (HOR) are platinum alloys. Similarly, at the air side of the fuel cell, platinum is the most efficient catalyst for the oxygen reduction reaction (ORR). To reduce the cost of the noble metal catalyst, though maintaining a high catalytic activity towards the HOR and ORR, small metal nanoparticles in the size range 1-5 nm are deposited or grown onto an electron-conducting and inert support material.[1, 2] The support material preferred due to its anchoring abilities is Vulcan XC-72 carbon black. Suitable electrochemical surface area (ESA) is obtained with platinum loadings of approximately 20 wt.%, for platinum supported by Vulcan XC-72 carbon black.[3]

At fuel cell operation the catalyst materials are subjected to very harsh conditions, such as low pH, high potential drop and a warm and humid environment, which is needed for the proton-conducting membrane to operate.

The catalyst aging and subsequent loss of efficiency are among other things due to the platinum nanoparticles agglomerating on the support material and corrosion of the carbon support material. As alternative to carbon black, nanostructures of carbon are being investigated for their use as support material for platinum and platinum-alloy nanoparticles. The highly ordered surface structure of carbon nanofibers (CNF) [4], carbon nanotubes (CNT) [5] and other nanostructured carbon materials give them high stability towards carbon corrosion, while the subsurface layers provide good electron-conductive properties. As the ordered surface structures provide resistance towards carbon corrosion, it is inadvertently equally more difficult to functionalize the carbon nanostructures with metal nanoparticles and to prepare catalyst inks without the use of auxiliary agents. This also affects the characterisation methods needed to compare these materials.

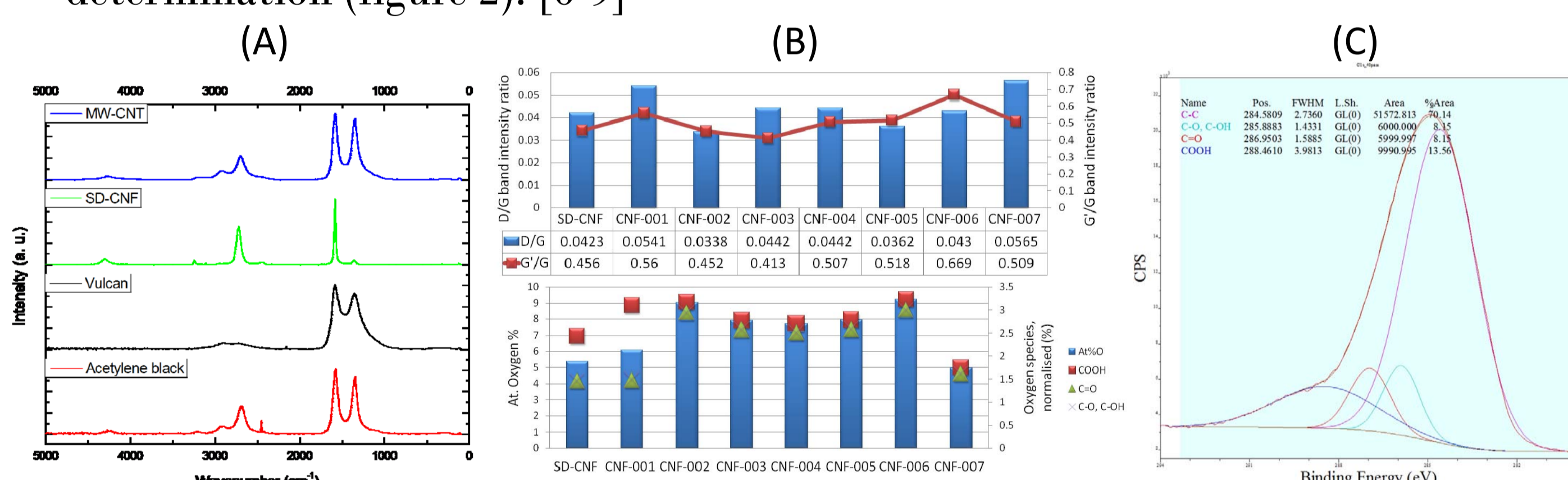


**Figure 1:** (A) show the first derivative ESR carbon signal of acid treated Showa Denko VgCF™, untreated Showa Denko CNF (SD-CNF) and an untreated multiwalled CNT sample (MW-CNT). (B) show the first derivative ESR carbon signal for untreated SD-CNF compared to acid treated fibres. On the left the fibres were treated in conc. sulphuric acid (GNF-001), 4M H<sub>2</sub>SO<sub>4</sub> (GNF-002), 2M HNO<sub>3</sub> (GNF-003) and 4M H<sub>2</sub>SO<sub>4</sub>/2M HNO<sub>3</sub> (GNF-004) for 2h at 90° C. On the right the fibres were treated in 4M H<sub>2</sub>SO<sub>4</sub> (GNF-005), 2M HNO<sub>3</sub> (GNF-006) and 4M H<sub>2</sub>SO<sub>4</sub>/2M HNO<sub>3</sub> (GNF-007) for 4h at 120° C. Most of the samples exhibit no noticeable change observed, except GNF-005, for which the electron conducting electron signal decreases, and GNF-007, for which it increases.

## Defect characterisation of carbon substrates

Electron spin resonance (ESR) spectroscopy relates the carbon signal the ratio between localised spins at structural irregularities and conduction carriers associated with electron conduction bands between graphene layers (figure 1). The measurements were performed with annealed (800°C) magnesium oxide as internal reference and diluting material.

Raman spectroscopy and X-ray photon spectroscopy (XPS) are surface sensitive spectroscopy methods used for CNT defect evaluation and carbon species determination (figure 2). [6-9]

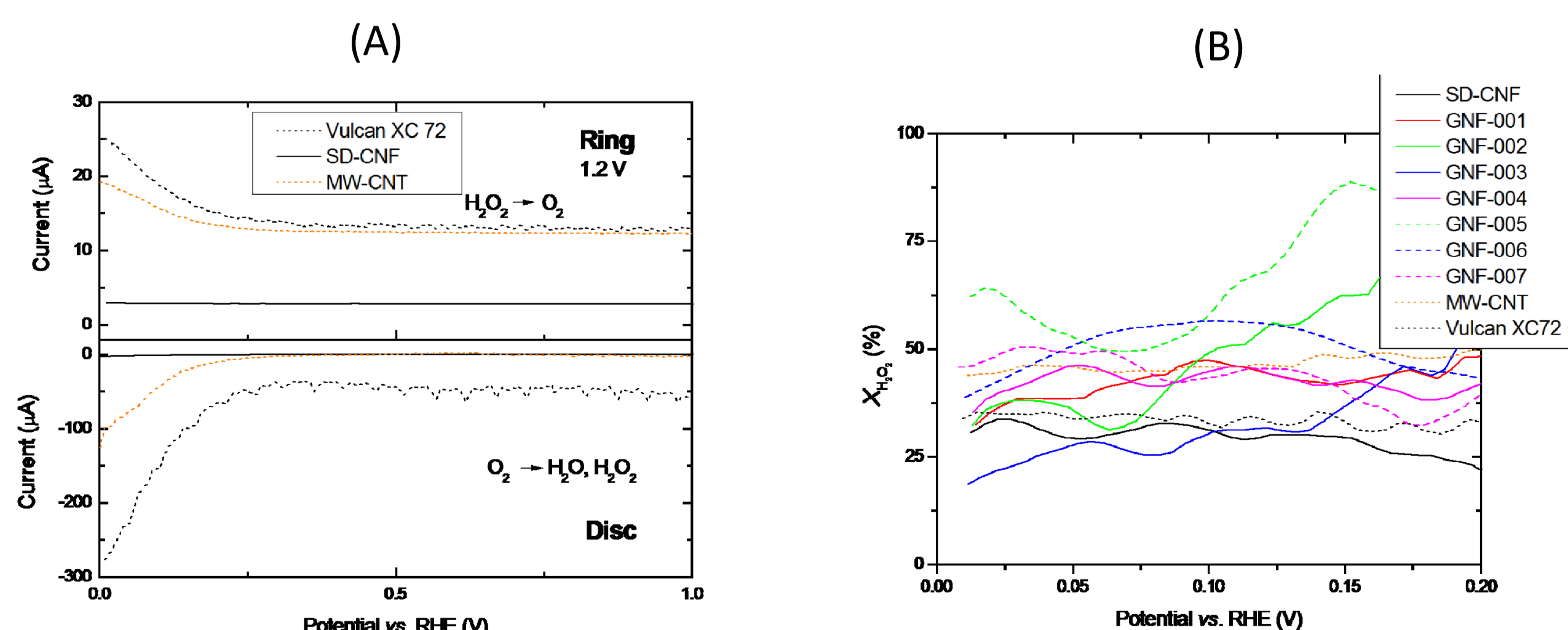


**Figure 2:** Differences in Raman spectroscopy signals obtained from Showa Denko CNF (SD-CNF), multiwalled carbon nanotubes (MW-CNT) and different types of carbon blacks (Vulcan and Acetylene black) can be seen in (A). The defect induced D-band (amorphous carbon) and G'-band (2D) intensity ratios vs. the respective G-band intensities are shown at the top graph of (B). The lower graph at (B) depicts the atomic oxygen content (in %) determined from XPS and the oxygen containing species evaluated by Gaussian peak fitting of the C 1s signal (example for SD-CNF shown at (C)). The peak fits are restricted and normalized with the total atomic oxygen content.

## Peroxide formation

For fuel cells the main transient species investigated is hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) formed during the ORR. Hydrogen peroxide breaks chemically down into hydroxyl radicals (OH•), which may cause membrane degradation and carbon corrosion.

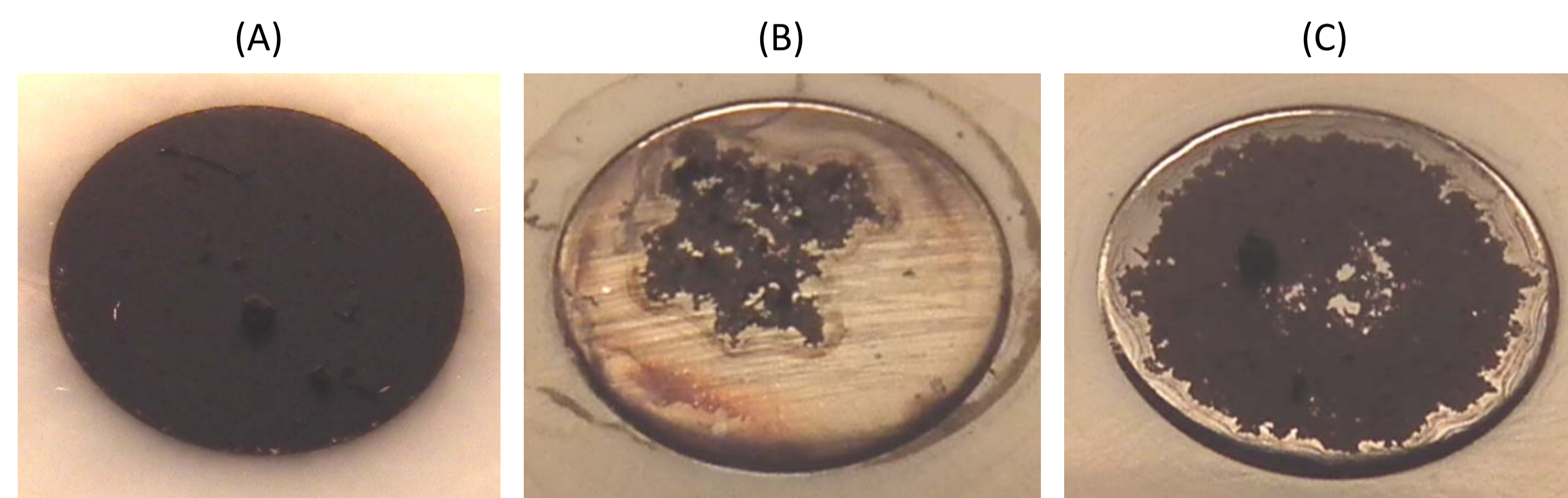
To evaluate the species produced during cell operation, the RRDE can be used to measure transient species formed during the potential sweep (figure 3).



**Figure 3:** (A) shows the current responses of the ring and disc of an RRDE for the positive-going (anodic) sweep with different carbon support materials attached to the glassy carbon disc electrode in 0.5 M HClO<sub>4</sub> (aq). The measurements are made in O<sub>2</sub> saturated electrolyte. The current responses for Ar saturated (0.5 M HClO<sub>4</sub> (aq.)) electrolyte has been subtracted. (B) shows the amount of hydrogen peroxide generated on the carbon supports is calculated from the Faradaic current response at the electrode ring. The disc potential is swept, whereas the ring potential is maintained at 1.2 V vs. DHE.

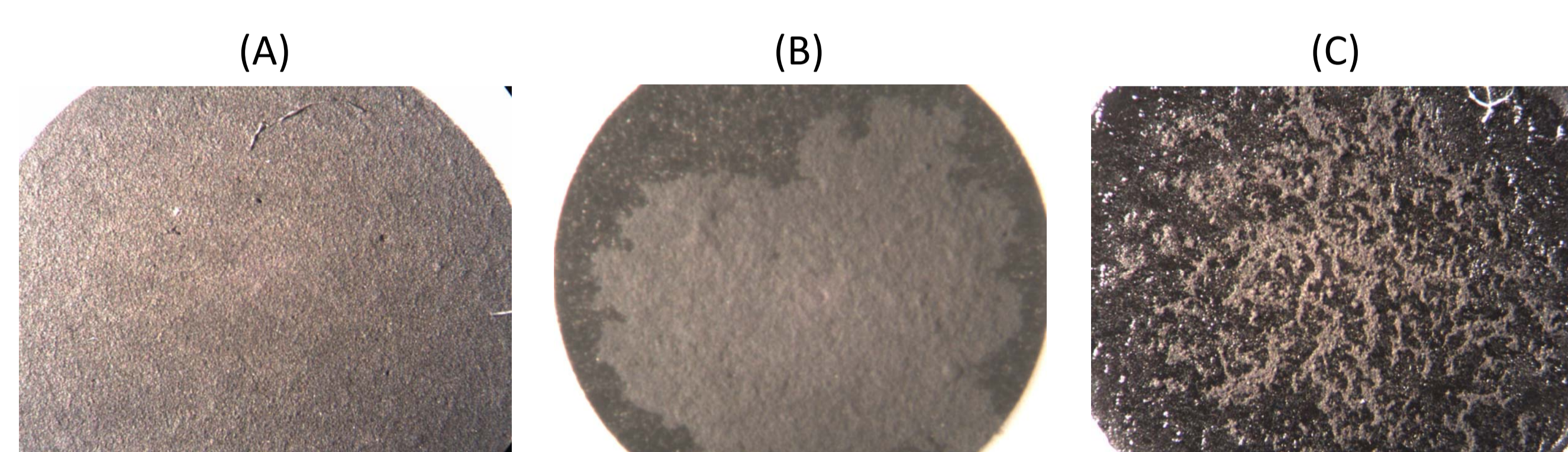
## Electrode preparation and dispersion properties

The preparation of the RDE and RRDE working electrodes, used for characterisation of fuel cell catalysts, is performed by preparation of a dispersion/ink, pipetting the desired amount and applying it to the electrode disc surface. Upon drying in inert atmosphere, a drop of Nafion® dispersion is applied and dried in order to form a <0.2 µm thick porous Nafion® layer (figure 4). [10] This electrode preparation method is very easily applicable with carbon blacks and carbon-black-supported catalyst. When this technique is employed on carbon nanostructured supports, the van der Waals attractive forces cause the support to agglomerate and form islands on the electrode surface. To be able to evaluate ORR effects properly the preparation of well dispersed catalyst on the electrode surfaces is needed, which presently proposes great challenges.



**Figure 4:** RDEs prepared by a two-step drop coating of catalyst and Nafion®. (A) shows that the carbon black supported platinum catalyst is well dispersed on the electrode surface. (B) shows that the gMWCNT-based catalyst agglomerate after application onto the glassy carbon electrode. (C) shows the same gMWCNT-based catalyst with PVP as dispersing agent.

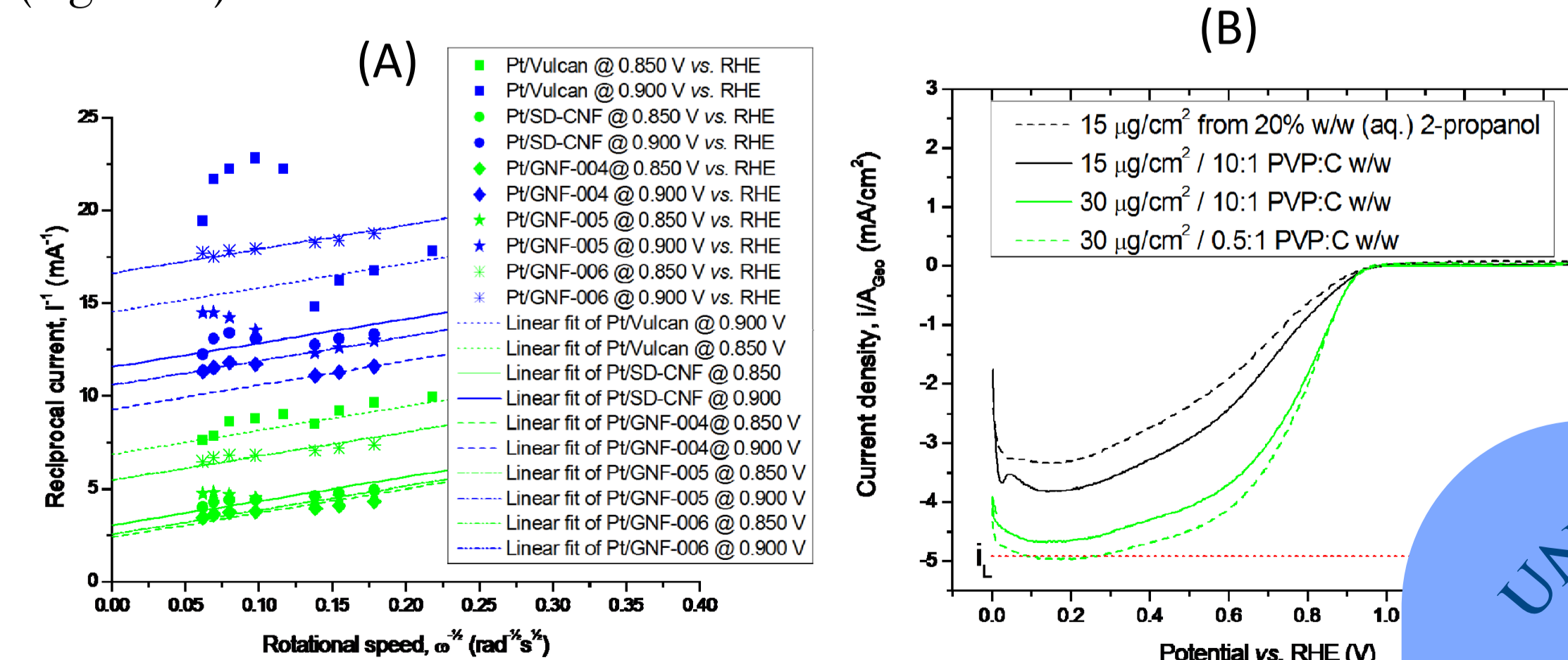
To disperse the different carbon nanostructured supports and supported materials different auxiliary agents such as solvents, dispersing agents and nano-halides can be used (figure 5).



**Figure 5:** Graphite discs, used to emulate glassy carbon disc electrodes. On these discs a drop of gCNF dispersed by different auxiliary agents has been put and dried. In (A) the dispersion was made in pure 1-propanol solvent, in (B) the graphitised CNF were dispersed in a 1:1 mixture of 2-propanol and water and in (C) the dispersion was made in water using polyvinyl pyrrolidone (PVP, k-36) as dispersing agent. The light areas are CNF, whereas the darker areas are the graphite disc substrate.

The best dispersion method is impossible to predict without an intricate study of the specific carbon support, as dispersion depends on any functionalisation which may affect the dispersion properties.

ORR kinetic properties have been investigated by using PVP for dispersion (figure 6).



**Figure 6:** (B) Koutecký-Levich plots of ORR in 0.5 M HClO<sub>4</sub> for different Pt/CNF catalysts at 0.9 V and 0.85 V vs. RHE. and Pt/Vulcan (BASf). The CNF samples are dispersed using PVP 0.5:1 w. ratio PVP:C. (A) Shows anodic ORR polarisation curves for a Pt/CNF catalyst dispersed under different conditions in O<sub>2</sub> saturated 0.5 M HClO<sub>4</sub> (aq.) electrolyte. The current responses under Ar have been subtracted.