THE ROLE OF DISPERSANTS IN MODIFYING THE CARBON NANOTUBE ELECTRODES FOR THE OXYGEN REDUCTION REACTION

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Abstract

Sodium dodecyl sulfate (SDS), sodium laureth sulfate (SLES), cocamidopropyl betaine (CAPB) and polyvinylpyrrolidone (PVP) have been chosen as dispersants in preparation of stable water suspensions of carbon nanotubes (CNTs). BET specific surface areas of buckypapers obtained by vacuum filtration of the suspensions are approximately 80 m^2/g and do not differ significantly from each other. Sheet resistance of backypapers obtained from the anionic and amphoteric surfactants (SDS, SLES and CAPB) were also close to each other and is in the range 0.5-0.6 Ω/sq. Only the use of PVP (polymeric dispersing agent) resulted in signifficant decrease of sheet resistance by two orders of magnitude. The heterogeneous electron transfer (HET) rate constant for hexacyanoferrate(III)/(II) and hexaamminoruthenium(III)/(II) redox couples was higher by one and more orders of magnitude on CNT electrodes treated with dispersants with respect to pristine CNTs. Adsorbed SDS, CAPB and PVP contributed to the slight lowering of onset potential of oxygen reduction reaction (ORR). From the point of view of ORR catalysis, the most promising dispersant agent is PVP. The CNT/PVP electrode showed the highest ORR limiting current and number of electron transfers close to four.

Keywords: Carbon nanotubes, dispersant agents, heterogeneous electron transfer, oxygen reduction reaction

1. INTRODUCTION

The high conductivity and chemical stability of sp^2 hybridized carbon materials make them good candidates as electrocatalysts in energy conversion devices, where fast charge transport and long-term operational stability are crucial. In particular, this applies to oxygen reduction reaction (ORR), which occurs at the cathode of fuel cells [1, 2] and air-metal batteries [3-5]. Electrocatalytic properties of carbon nanotubes can be tailored to ORR by doping [6]. However, ink formulation and unifomity of catalyst layer play crucial role in catalysis of ORR [7, 8]. The structure of douple layer and charging dynamics is also of great importance for electrode performance [9]. As we have shown in Ref. [10], the residues of dispersant molecules adsorbed on nanotubes can change the structure of the electrode/electrolyte interface. Molecules of sodium dodecyl sulfate (SDS) adsorbed on graphene have contributed to better wettability of graphene surface making it more accesible to O_2 [11]. Poly (vinyl pyrrolidone) (PVP) has been used as an effective dispersant of carbon nanotubes, because the polymer chains wrap the nanotubes and and weaken the interactions between them [12].

The influence of dispersant residues permanently adsorbed on carbon nanotubes on their catalytic properties is still not sufficiently explored. This was the main motivation for taking up this topic. For this study, we have chosen SDS and SLES, which are ionic surfactants, cocamidopropyl betaine (CAPB), which is an amphoteric surfactant commonly used as mild cleaning agent in body care products [13] and PVP, which is a polymeric

dispersing agent commonly used by commercial CNT suppliers for delivery of the stable CNT dispersions in water [14]. Buckypapers prepared by vacuum filtration from water dispersions containing the mentioned above dispesants were subjected to BET analyses and surface resistance measurements. For electrochemical measurements, glassy carbon electrodes modified with carbon nanotubes were used.

2. METHODS

2.1 Materials

Multi-walled carbon nanotubes (CNT) with diameters of 10-30um, lengths of 5-20um and purity of 99% by weight, were supplied by Institute of Carbon Technologies Sp. z o. o. (Toruń, Poland). SDS, SLES, CAPB and PVP (98% purity) were delivered by Sigma Aldrich.

2.2 Preparation of CNT water dispersions and CNT films

Dispersions of CNTs were prepared by ultrasonication for 60 min of mixtures of CNTs with a concentration of 0.2 wt% in 1 wt% aqueous solution of SDS, SLES, CAPB and PVP. The suspensions were vacually filtered through a polycarbonate membrane (Millipore ATTP04700, Merck KGaA, Germany) with a pore diameter of 0.8 μm and purged with distilled water. CNT deposit collected on the filter were vacuum dried at 50°C for 7h.

2.3 Characterization of CNT films

The specific surface areas (SBET) of the CNT deposites were determined using the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.02-0.2 using an ASAP 2010 automated adsorption instrument (Micromeritics, Norcross, GA, USA). Electrical sheet resistance measurements were performed on the films deposited on the filters by the four-point method using a Keithley 2450 source measure unit.

2.4 Electrochemical measuremets

Electrochemical measuremets were carried out in three electrode configuration. As a working electode served 4 mm diameter glassy carbon disc electrode onto which the CNT materials were applied in the form of inks. Inks were prepared by dissolving CNT deposites in a mixture of distilled water, ethanol, and Nafion. A Pt plate was used as a counter electrde and Ag/AgCl electrode served as the reference electrode, respectively. Cyclic voltammograms (CV) and linear sweep voltamograms (LSV) were recorded using a VIONIC potentiostat (Metrohm AG, Switzerland).

To evaluate catalytic activity of CNTs, two benchmark redox probes were subjeted to electrchemical tests: $[Fe(CN)_6]^{3-/4-}$ (0.5 mM) and $[Ru(NH_3)_6]^{3+/2+}$ (1 mM) in 0.5 M KOH supporting electrolyte. LSVs of ORR were recorded in O_2 saturated 0.1 M KOH aqueous solution at a scan rate of 5 mV/s on rotating disk electrode RDE. The rotation speed ranged between 800 and 2800 rpm. Koutecký-Levich (K-L) analysis was used for detmining the number of electrons trasnferred [15].

3. RESULTS

Surface area BET and sheet resistance of carbon nanotube films are compared in **Table 1**. Surface area do not differ signifficantly from each other. The lowest surface area had CNT films obtained in the presence of CAPB (68.6 m^2/g), and the best developed surface had CNT/SLES (87.8 m^2/g).

Dispersant agents have positive effect on electrical conductivity. Sheet resisntance of CNT films obtained from water dispersions with SDS, SLES and CAPB is more than five times lower than sheet resistance of CNT film prepared from dipersion in pure water (3.36 Ω/sq). The most significant decrease in resistance was observed in film with PVP. The sheet resistance of 6.3 mΩ/sq is one hundred times lower than in films obtained using surfactants.

Table 1 Surface area BET and sheet resistance of CNT films obtained from water suspensions with different disparsants

Material	S_{BET} (m^2/g)	Sheet resistance (Ω/sq)
CNT	79	3.36
CNT/SDS	75.93	0.62
CNT/SLES	87.79	0.51
CNT/CAPB	68.64	0.53
CNT/PVP	83.15	0.0063

In **Figure 1**, we compare the cyclic voltammograms of $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ measured on glassy carbon electrode modified with CNTs, which were previously treated with SDS, SLES, CAPB and PVP. The influence of dispersants on the catalytic activity of nanotubes is apparent and is manifested by changes in anodic and cathodic peak currents as well as by anodic and cathodic peak separation.

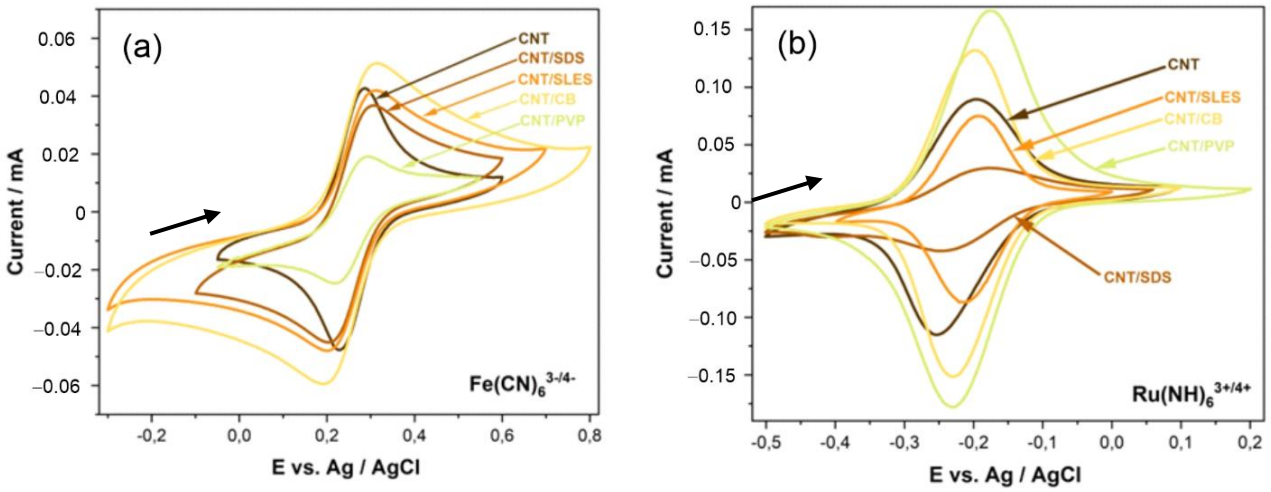

Figure 1 CVs of 0.5 mM $Fe(CN)_6^{3-/4-}$ **(a)** and 1.0 mM $Ru(NH_3)_6^{3+/2+}$ **(b)** redox couples in 0.5 M KCl aqueous solution as a supporting electrolyte on CNTs obtained from the pure water suspensions (CNT) and water suspensions with SDS, SLES, CAPB and PVP at scan rate of 20 $mV \cdot s^{-1}$.

Based on the anodic and cathodic peak separation, we have calculated heterogeneous electron transfer (HET) rate constant, k_0, which is the basic parameter determining electrocatalytic activity of electrode materials. Results of calculations based on Nicholson procedure [16, 17], which was extended by Klinger and Kochi [18-20], are listed in **Table 2**.

The charge transfer coefficient (α) remains close to 0.5 for both redox mediators, suggesting a symmetrical energy barrier both for oxidation and reduction. Unmodified carbon nanotubes show rather low electrocatalytic activity, what is manifersted by low HET rate constants of 3.6×10^{-5} cm/s and 6.8×10^{-5} cm/s for $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$, respectively. CNTs treated with surfactants (SDS, SLES and CAPB) exhibit much better kinetics. For ferro-/ferricyanide redox couple, the k_0 increases 20 times on CNT/SDS and CNT/SLES electrode. In the case of the CNT/CAPB electrode, an almost eight-fold increase in k_0 is observed. On the other hand, the treatment with PVP does not affect the k_0 at all.

The influence of dispersants is much greater on the electrocatalysis of the redox reactions of hexaammineruthenium (II)/(III) redox couple. CNTs treated with SDS show a slight increase in k_0, which is doubled compared to pristine CNTs. However treatment with SLES and CAPB leads to a more than 50-fold

increase in the k_0 value. Opposite to $Fe(CN)_6^{3-/4-}$ redox medium, CNTs modified with polymer dispersant (PVP) also show an excellent activity to catalysis of redox reactions of $Ru(NH_3)_6^{3+/2+}$. HET rate constant increases almost forty-fold compared to unmodified CNTs.

Table 2 Comparision of the charge transfer coefficient, α, and the HET rate constants, k_a.

Buckypaper Electrode	$Fe(CN)_6^{3-/4-}$		$Ru(NH3)_6^{3+/2+}$	
	α	k_0 [10^{-4} cm s^{-1}]	α	k_0 [10^{-4} cm s^{-1}]
CNT	0,485	0,36	0,475	0,68
CNT/SDS	0,493	6,27	0,539	1,41
CNT/SLES	0,494	6,19	0,486	40,2
CNT/CAPB	0,506	2,73	0,453	36,2
CNT/PVP	0,505	0,36	0,438	25,9

In **Figure 2a**, we show LSV curves of ORR recorded on RDE electrode modified with CNTs treated with dispersant agents. In all LSV curves three regions are distinguished, which can be assigned to different processes. First part of the LSV curve above 0.75 V vs. RHE is the kinetic-controlled region, in which the ORR is sluggish. The second part between 0.75 and 0.6 V refer to the mixed kinetic and diffusion-controlled region, in which rapid increase of the ORR current is observed. The third part between 0.55 and 0.4 V is the plateau region, in which the diffusion controlled process occurs [21]. In analyses of the LSV curves, we considered such parameters of LSV curves, as onset potential (E_{onset}) determined by tangential method and the steady-state limiting current density (j_{lim}) determined from the diffusion-limiting region of the ORR-LSV curve.

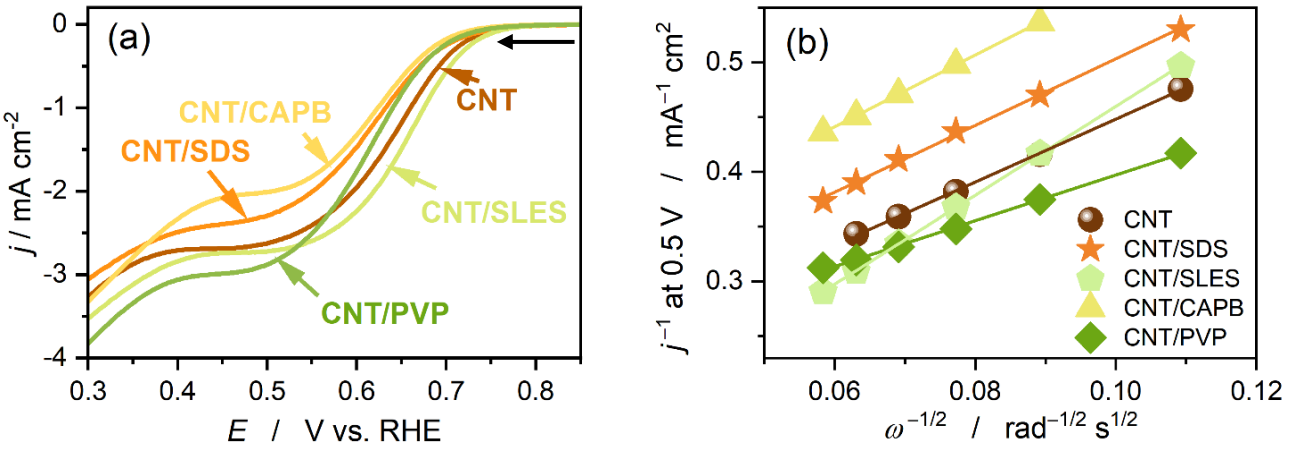

Figure 2 (a) LSV curves recorded in O_2-saturated 0.1M KOH solution at a scan rate of 5mVs^{-1} and rotation speed of 1600rpm. **(b)** Koutecky-Levich plots for current densities at potential 0.5V and RDE rotation rate ranged between 800 and 2800 rpm.

All dispersants except SLES contribute to the lowering of the onset potential of ORR. This is an undesirable effect – it means a higher overpotential is needed for the ORR to occur. For comparison, the onset potential on the Pt/C electrode is 0.9 V vs. RHE. It should be noted, however, that the differences are insignificant, no more than 0.03 V. Dispersants also influence the limiting current. This is particularly evident in the case of SLES, which causes a 25% limiting current drop. On the other hand, the PVP contributes to an increase in limiting current by over 10%.

Table 3 Comparision of the onset potential for ORR, E_{onset}, the limiting current, j_{lim}, the slope of the Koutecki-Levich plot and calculated number of electrons transfered, n_{KL}.

Electrode	E_{onset} / V vs. RHE	j_{lim} / mA cm^{-2}	KL slope	n_{KL}
CNT	0.718	2.645	2.875	3.02
CNT/SDS	0.698	2.268	3.048	2.85
CNT/SLES	0.726	2.700	4.062	2,14
CNT/CAPB	0.695	1.958	3.277	2.65
CNT/PVP	0.692	2.916	2.356	3.68

In this study, we also estimated the number of electron transfers involved during the ORR. The diffusion-limited current densities over the RDE rotation rate are shown in the form of Koutecki-Levich plots in **Figure 2b**. Slopes of the Koutecki-Levich plots and corresponding n_{KL} values are listed in **Table 3**. The number of electron transfers on CNT depends strongly on the treatment with dispersants. In general, n_{KL} decreases after treatment of carbon nanotubes with surfactants (SDS, SLES, CAPB). This suggests that the four electron ORR reaction pathway is incomplete. On the other hand, the CNT electrodes treated with PVP promote the four electron ORR reaction, what is manifested by increased number of transferred electrons with respect to the pristine CNTs.

4. CONCLUSION

In this study we have compared electrocatalytic properties of CNT electrodes treated with surfactants (SDS, SLES and CAPB) and polymeric dispersant agent (PVP). Influence of dispersants on electrocatalytic properties of CNTs is apparent. HET rate constant of ferro-/ferricyanide and hexaammineruthenium (II)/(III) redox couples increases by more than one order of magnitude on CNT electrodes treated with dispersants. SDS, SLES and CAPB have a slight negative effect on ORR catalysis, which manifests itself in a reduction of the ORR onset potential and the limiting current. The exception is the polymer dispersant agent, PVP, which contributes to increasing the limiting current and promoting the four-electron reaction pathway on CNT electrode.

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