ELECTROCHEMICAL BEHAVIOR OF ACTIVATED CARBON BLACKS

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ABSTRACT
Carbon black (Cabot Corporation) was activated using three different activators: sulfuric acid, sodium hydroxide and hydrogen peroxide. The electrochemical activity of activated carbon black was investigated in acidic solution by cyclic voltammetry and linear sweep voltammetry. The effect of anodic potential limit on the activity and stability of activated carbon black electrode in the hydrogen evolution region was evident. The highest activity for hydrogen evolution reaction was recorded for carbon black activated with hydrogen peroxide.

INTRODUCTION
Carbon black is often used as a support material for electrocatalyst. Although new forms of carbon, such as carbon nanotubes and graphene, are also investigated, carbon black remains major support material. The effect of the surface chemical properties of carbon black on their electrochemical performances has been studied [1]. There are surface functional groups at the surface of carbon black: carboxylic anhydride, carboxylic acid, lactone, lactol, phenol carbonyl, and quinone [2]. The groups are an important feature of carbon black influencing their electrochemical properties as well as their ability to act as a support for electrocatalyst.

The type and the number of surface groups present on the surface of carbon black can be altered by the activation agent. Treatment of carbon black with different activating agents such as HNO_3 or H_2O_2 introduces different oxygen-containing groups at the surface of carbon black. So far, the usage of concentrated activators was investigated. The effect of oxidizing conditions was more thoroughly investigated for adder forms of carbon. It was found that the concentration of acid strongly influences the surface chemical composition of graphene [3].

This investigation aimed to compare the effect of different activators of a medium concentration on carbon black. Three different activators were used: sulfuric acid, sodium hydroxide and hydrogen peroxide with a concentration of 5 mol dm^{-3}. The electrochemistry behavior of activated carbon black was investigated in acid solution.

METHODS
The surface properties of the carbon black Vulcan XC-72 (Cabot Corporation) were altered by oxidizing agents: a) sulfuric acid; b) sodium hydroxide and c) hydrogen peroxide. The same procedure was employed with all three activators: solid to liquid ratio was 1:100, the concentration of activator was 5 M, the temperature of activation was 50 ^oC, and the time of activation was 3h. The activated carbon was separated from the reaction mixture, washed with distilled water, and dried at 80^oC overnight. The obtained samples were designated as CB (unaltered carbon black), CB-H_2SO_4 (activated with H_2SO_4), CB-NaOH (activated with NaOH), and CB-H_2O_2 (activated with H_2O_2).

The activated samples were used to prepare catalytic ink with 5%wt Nafion. Catalytic ink was applied to the surface of the glassy carbon electrode (a diameter of 3 mm) and left to dry at room temperature. A modified glassy carbon electrode was used as the working electrode and designated in the same manner as the samples. For the sake of comparison glassy carbon electrode modified with

unaltered carbon black (CB) was also recorded under the same conditions. The electrochemical experiments were performed in a three-electrode glass cell using an Autolab PGSTAT302N (Metrohm - Autolab BV, Netherlands) with reference electrode Ag/AgCl in 3 M KCl and a platinum rod as a counter electrode. The method of cyclic voltammetry (CV) was used with a scan rate of 100 mV s^{-1}. Linear sweep voltammetry (LSV) was applied with the scan rate of 5 mV s^{-1}.

RESULTS AND DISCUSSION

The behavior of carbon support in the hydrogen evolution area is important for the development of better metal support as well as for the investigation of the metal-free electrocatalyst. The surface groups of carbon black can exhibit a significant influence on their behavior. The initial investigation of activated carbon blacks was performed by cyclic voltammetry. To assess the influence of oxidation on the activity of activated carbons toward hydrogen evolution reaction (HER) the effect of the anodic potential range was studied. Cyclic voltammograms were recorded in the potential range -1.2 V to +1.6 V and -1.2 V to +1.0 V (**Figure 1.**)

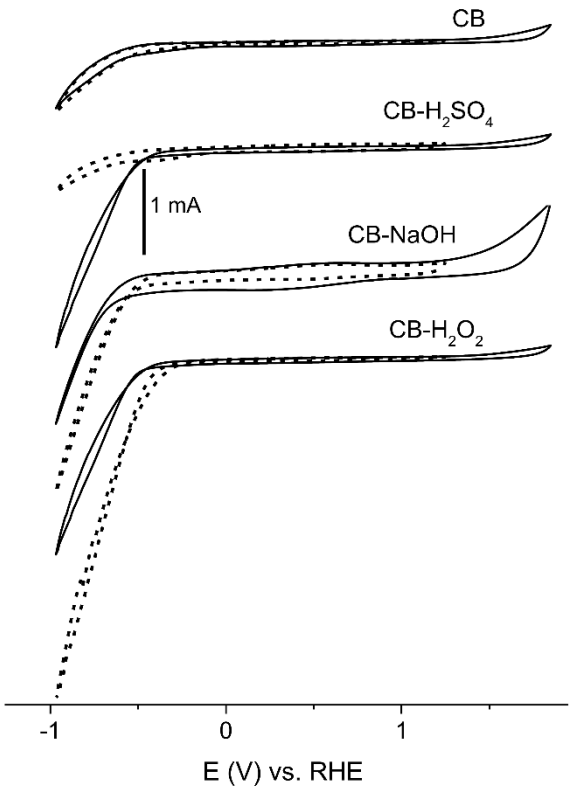

Figure 1. Cyclic voltammograms of original carbon black (CB), and activated carbon blacks samples recorded in 0.1 M H_2SO_4 at scan rate of 100 mVs^{-1} in potential range -1.2 V to +1.6 V (solid curve) and -1.2 V to +1.0 V (dashed curve)

No noticeable effect of anodic potential limit was noted for the original sample, CB. All three activated samples showed higher HER current than the original CB after the cycling up to +1.6 V. The hydrogen evolution current was significantly higher when CB-H_2SO_4 was cycled up to 1.6 V, while CB-NaOH and CB-H_2O_2 exhibited lower HER currents. Noticed effects can be ascribed to the increased (for CB-H_2SO_4) or decreased (CB-NaOH and CB-H_2O_2) number of available HER sites after oxidation treatment [1]. CB-NaOH sample showed the highest value of capacitive current as well as the highest value of oxygen evolution current. The values of capacitive currents were further

increased after an increase in the anodic potential limit. It is considered that the presence of oxygen functional groups at the surface of the activated carbon reduces their hydrophobicity and increases their capacitancde [4].

The activity of activated carbon blacks toward hydrogen evolution reaction was investigated by linear sweep voltammetry in the potential range 0.0 V to -1.2 V (**Figure 2a**).

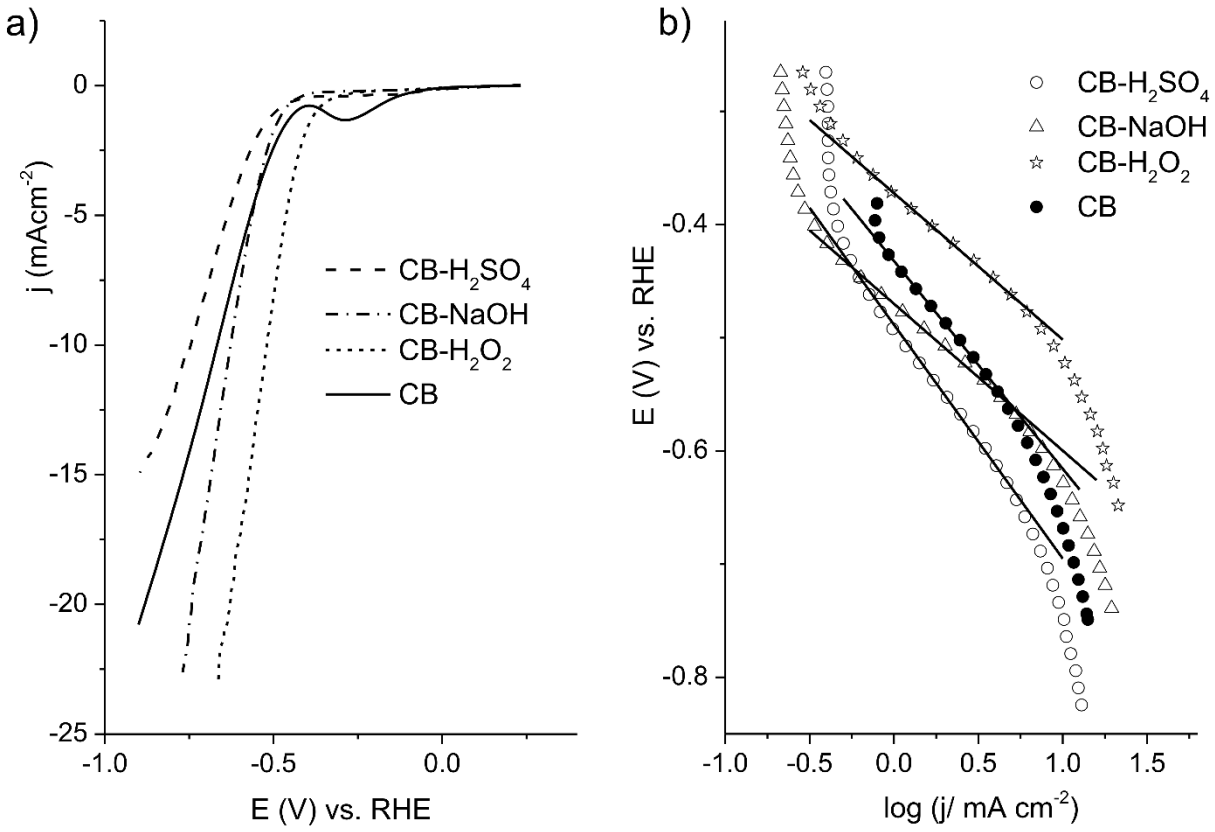

Figure 2. a) Linear sweep voltammograms recorded in 0.1 M H_2SO_4 at scan rate 5 mVs^{-1}; b) Tafel plots of unaltered and activated carbon black samples.

The highest activity for HER was recorded for CB-H_2O_2. The sample CB-NaOH showed higher HER currents than CB at a potential lower than -0.8 V. The obtained onset potentials were -0.66 V for CB, -0.71 V for CB-H_2SO_4, -0.69 V for CB-NaOH and -0.59 V for CB-H_2O_2. The most positive onset potential was obtained for CB-H_2O_2 showing an improved surface for HER.

Further study of HER activity of activated carbon blacks was performed by the Tafel plots (**Figure 2b**). The Tafel slopes of -180 mV dec^{-1} for CB, -208 mV dec^{-1} for CB-H_2SO_4, -129 mV dec^{-1} for CB-NaOH and -129 mV dec^{-1} for CB-H_2O_2 were obtained. Tafel slopes of values of 120, 40 and 30 mV dec^{-1} are expected for the Volmer, Heyrovsky and Tafel rate determining steps, respectively. Much higher values of Tafel slope for carbon materials, as obtained in this work, are often reported in literature [1,5]. HER mechanism for metal-free electrocatalyst is not completely understood. Nevertheless, it can be concluded that the activation of carbon black with NaOH and H_2O_2 resulted in a lower Tafel slope than the original CB indicating a lower energy barrier for HER [6].

CONCLUSION

The influence of the activation procedure on the electrochemical behavior of carbon black was investigated. Relatively mild activation conditions were used. Activation of carbon black was performed with 5 M H_2SO_4, NaOH and H_2O_2. The influence of oxidation on the electrochemical properties of samples was tested by varying anodic potential limits. Samples modified with H_2O_2 and NaOH showed diminished HER current when the anodic potential limit was set to higher values. These two samples also showed lower values of the Tafel slope. The highest activity toward hydrogen evolution reaction was recorded for the carbon black sample activated with H_2O_2.

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