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Pd/C-Based Sensor for Gas Sensing in Transformer Oil

Haidan Lin [1], Jiachang Guo [1], Daiyong Yang [2], Shouxue Li [1], Dan Liu [2], Changyan Liu [1], Zilong Zhang [3], Bolin Wang [3,*] and Haifeng Zhang [3,*]

[1] Electric Power Research Institute, State Grid Jilin Electric Power Co., Ltd., Changchun 130012, China; a125790709@163.com (H.L.); 1325377991@163.com (J.G.); x13629890704@163.com (S.L.); w8551191546@163.com (C.L.)
[2] Jilin Electric Power Research Institute Co., Ltd., Changchun 130012, China; sr17662744213@163.com (D.Y.); a1772681@163.com (D.L.)
[3] School of Chemical Engineering, Northeast Electric Power University, Jilin 132012, China; zilongzhang_neepu@163.com
* Correspondence: bolinwang@neepu.edu.cn (B.W.); zhfeepu@163.com (H.Z.)

Abstract: The detection of dissolved gas in transformer oil is of vital importance to diagnose the early fault and monitor the security and stability of power systems. In this work, distinct Pd/C, Pd/C-R and Pd/NC were synthesized and evaluated. XRD and XPS characterizations show that both Pd^0 and Pd^{II} are presented over the surface of carbon host for Pd/C, while poor gas-sensitive properties were presented for Pd^0 in H_2-reduced Pd/C-R sample. High content of cationic Pd^{II} species are synthesized by nitrogen doping of the carbon surface for Pd/NC. The experimental results showed that the gas-sensitive performances of H_2/CO/C_2H_2 gases is facilitated over the developed Pd/NC material. This study can provide reference for the rapid detection and fault diagnosis of faulty gases in transformers.

Keywords: dissolved gas; transformer oil; Pd/C; XRD and XPS characterization; gas-sensitive

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1. Introduction

Transformer is a static induction appliance that uses the principle of electromagnetic induction to change AC voltage and transmit AC power, and is widely used in the electrical field [1–3]. Since transformer oil consists of hydrocarbons, some C–C and C–H bonds break into a small number of reactive hydrogen atoms and free radicals of unstable hydrocarbons [4,5], forming hydrogen (H_2) and low molecular hydrocarbon gases such as methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6) and other decomposition products. One of the keys to ensuring the safety of power grid operation, improving equipment utilization, and lowering maintenance and overhaul costs is the timely and accurate prediction of latent faults in power transformers, real-time inspection of transformer insulation status, and determination of transformer fault types [6–8]. Therefore, it is essential to monitor the proper operation of the online transformers by detecting the main components of transformer oil decomposition gas. Dissolved gas analysis (DGA) has evolved into an efficient and practical method for tracking the status of a transformer's operation and identifying its fault types to ensure its safe and reliable operation [9].

Conductor gas-sensitive sensors are influenced by the combination of morphological structure and electron motion, e.g., crystal structure, particle size, dimensionality, morphology, specific surface area, etc. [10–12]. Palladium (Pd) catalysts have been chosen as the preferred material for the preparation of thin sensor films or dopants to modulate their active surfaces, and much work has been done to develop sensing materials with good electrical response to detect target gases or adsorbents with strong adsorption capacity to remove these impurities. Given its very enormous specific surface area and distinctive physical and chemical characteristics, carbon material is frequently used to combine with other metals to create new materials or to improve performance [13,14]. Recent years,

Carbon supported noble metals-based materials have been widely used in gas-sensitive sensing. Pd/C gas-sensitive sensors are inexpensive to prepare, easy to implement, and have potential industrialization prospects. In addition, Pd/C material is sensitive to the seven fault characteristic gases such as H_2, CO, CO_2, CH_4, C_2H_4, C_2H_2 and C_2H_6 dissolved in transformer oil, which has been currently an important material for preparing gas sensors [15–17]. However, the properties of Pd/C sensors, such as poor selectivity, low sensitivity, easy poisoning, short life span, and susceptibility to interference by external factors, have seriously restricted its use and development. In light of its use in online monitoring equipment for oil dissolved gases, Pd/C-based semiconductor materials' investigation of gas-sensitive features is crucial [18,19].

In existing research, improving the gas sensing performance of materials through technical strategies such as morphology modification, doping with precious metals, non-precious metals, non-metals or metal oxides, and catalyst addition has gradually been proven to be an important technical means to improve the gas sensing performance of materials. In this work, the effect of the respective modifications of Pd and carbon hosts on the gas sensing performance is investigated and it is found that nitrogen doping can improve the sensing performance of non-metallic elemental carbon, as well as change the electronic structure and chemical properties of the carbon material, thus improving its sensing performance. The present work provides theoretical support for the study of gas monitoring of partial discharge in transformers.

2. Results and Discussions

2.1. Structural Characterization

In this work, the performance of Pd/C, Pd/C-R, and Pd/NC in gas sensing was examined. The samples' XRD patterns were shown in Figure 1. The carbon host's amorphous peaks (002, 100) were the only metallic Pd crystals to form in the Pd/C, according to X-ray diffraction (XRD) study. This work, Pd/C, Pd/C-R and Pd/NC were studied and evaluated their performance in Gas Sensing. It demonstrated that the active components are highly dispersed on the surface of host. It is common that when supported active components are characterized by XRD, the diffraction peaks of the active components cannot be found on the XRD patterns. In general, it is suggested that the active components in the Pd/C sample are in such a small quantity or an amorphous state that they evade the detection by X-ray diffraction. However, for the sample of Pd/C-R, significant metallic Pd crystals were observed via the reduction treatment of Pd/C in H_2 as shown in Figure 2 [20]. The co-existence of Pd^{2+} and Pd^0 in the Pd/C, and the presence of Pd^0 in Pd/C-R can be verified by the flowing XPS analysis. All survey XPS spectra (Figures S1 and S2) and atomic percentages (Tables S1 and S2) are presented in Supplementary Materials. When the carbon was dopped with N (Figure S3), we can clearly see that highly dispersed Pd species were generated, since no significant metallic Pd crystals were formed in the Pd/NC.

2.2. Gas-Sensitive Tests

The Response-current and Response-recovery tests were investigated to reveal the effect of Pd/C-based gas-sensitive materials on the gas-sensitive performance of the three characteristic gases (H_2, CO, C_2H_2) in a typical transformer oil.

2.2.1. Response-Current Tests

One of the most significant factors influencing the operational performance of gas sensitive materials and gas sensors is the operating current (operating temperature). Typically, at room temperature, gas sensitive materials and gas sensors exhibit little or very little sensitivity to the measured gas. The gas-sensitive element has an optimal operating current for each gas, i.e., a current at which the sensitivity response is maximized. In general, there is a range of operating currents. The best operating current must be obtained before doing further tests. Therefore, we have tested the sensitivity of the prepared parothermal gas sensors for H_2, CO and C_2H_2 gases at 160 μL/L as a function of current.

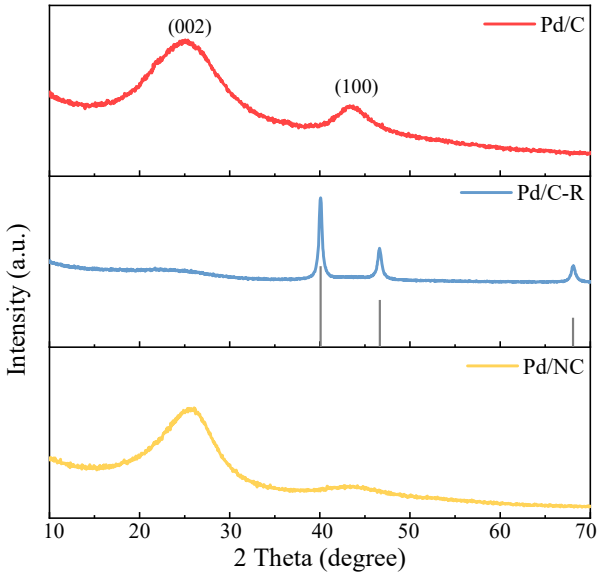


Figure 1. X-ray diffraction patterns of Pd/C, Pd/C-R and Pd/NC.

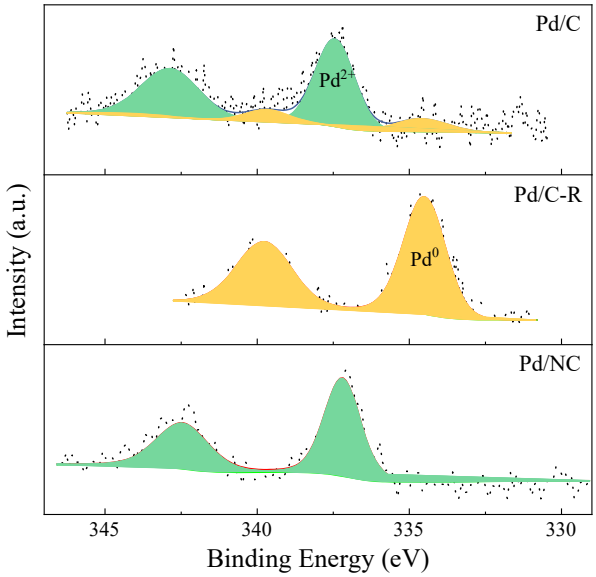


Figure 2. X-ray photoelectron spectra of Pd/C, Pd/C-R and Pd/NC.

The operating current range of 80–140 mA was selected for the following tests and analysis, considering the conventional testing conditions in this field. The sensitivity of the evaluated sample to H_2 was perturbed, showing an increasing and then decreasing trend as the current increases as shown in Figure 3a. The sensitivity of the gas detecting element will drop when the working current is low, which is a significant occurrence. Low electrical signals occur from the surface active components of gas sensitive materials being insufficient to properly interact with the gas through the electronic exchange. Given the strong reducibility of H_2, it is excited at a faster rate when reacting with Pd sites under high temperature conditions. After the working current surpasses the ideal working current, the rate of drop in molecule concentration on the material's surface is substantially accelerated, exhibiting a decrease in sensitivity. It can be clearly observed that the sensitivity current characteristic curve of Pd/C-R is located at the bottom of all evaluation sample performance curves. The center of the optimal working current is 110 milliamperes, corresponding to a sensitivity of 7.76. On the contrary, the sensitivity current curves of Pd/C and Pd/NC materials were located at the top of the performance region, and exhibit the sensitivities of 10.12 and 13.51, respectively under the working current constraint of 110 mA. The

synergistic interaction of the surface nitrogen species and cationic Pd results in a clearly enhanced performance of the Pd/NC material.

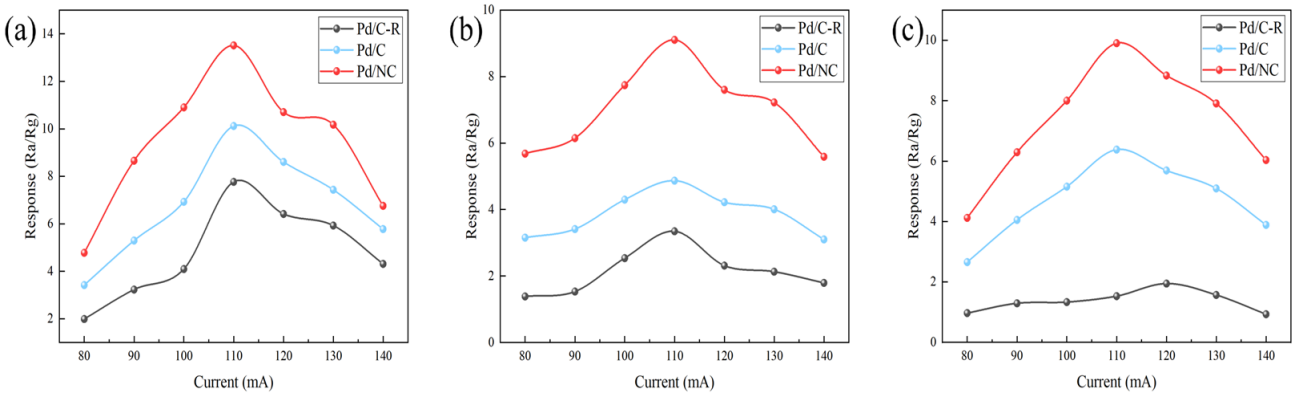


Figure 3. (**a**) Gas responses of Pd/C-based materials gas sensors to 160 μL/L H_2 at different working current; (**b**) Gas responses of Pd/C-based materials gas sensors to 160 μL/L CO at different working current; (**c**) Gas responses of Pd/C-based materials gas sensors to 160 μL/L C_2H_2 at different working current.

In the discussion of CO gas testing below, the operating current range of 80–140 mA is selected. As can be seen in Figure 3b, the sensitivity of the evaluated sensor exhibits a rising and then decreasing phenomenon with increasing current intensity. A trend of gas-sensitive performance similar to that of H_2 was presented, indicating higher scalability advantage of the developed Pd/C-based material. We can see that the sensitivity-current performance of Pd/C-R was operated at a low level, generating an optimal operating current of 110 mA. The response-current curve for Pd/C and Pd/NC were located at the top of the performance region, generating the sensitivity of 4.87 and 9.10, respectively. Similar to the aforementioned sample, the provided characteristic curves do not cross, showing that the surface N alteration considerably increased the Pd/NC material's gas sensitivity over the whole monitoring range.

The sensitivity of the developed materials for C_2H_2 rises and then falls with the increasing current as shown in Figure 3c. The response-current characteristic curve for Pd/C-R was at the bottom of the figure, where the best operating current was 110 mA, corresponding to a sensitivity of 1.95. Surprisingly, the sensitivity-current curve for cationic Pd materials (Pd/C and Pd/NC) were facilitated, and the optimal operating current was 110 mA, tested at the sensitivity of 6.37 and 9.91, respectively. The performance curves of the investigated materials failed to cross, following the same tendencies shown for the first two gases. It goes without saying that the N-modification considerably improves the performance of the Pd/C-based materials. The response-current characteristic curves of Pd/C-based materials under H_2, CO and C_2H_2 atmospheres show the following features: the operating current increases first and then decreases. The outstanding gas-sensitive performance of Pd/NC suggests that the addition of cationic Pd and N species aided the gas-sensitive performance and that the doping method has a significant impact on the material's gas-sensitive performance. The obtained sensitivity is H_2 > C_2H_2 > CO.

2.2.2. Response-Recovery Tests

Response-recovery time is a strong descriptor for efficient assessment and identification the evaluated gases. Based on the previous obtained data, the response-recovery properties of the three gases were tested at the optimum operating currents for the aforementioned materials, and the curves are shown in Figure 4.

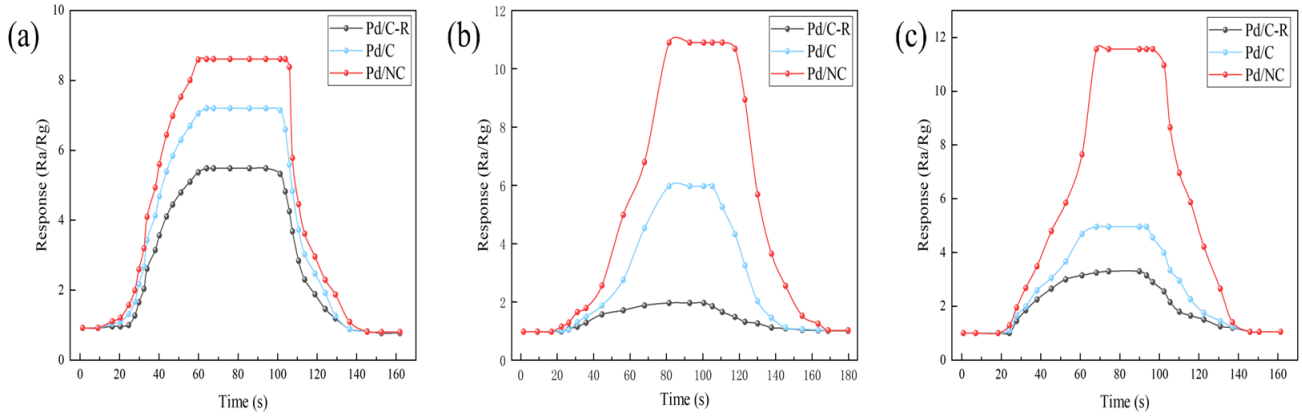


Figure 4. (**a**) Response-recovery curve of Pd/C-based materials gas sensor to 160 μL/L H_2; (**b**) Response-recovery curve of Pd/C-based materials gas sensor to 160 μL/L CO; (**c**) Response-recovery curve of Pd/C-based materials gas sensor to 160 μL/L C_2H_2.

It can be seen from Figure 4a that the H_2 starts to diffuse within the material surface and the pores, showing different diffusion behavior when H_2 is introduced. When the gas channel is fully established, all the evaluated materials respond quickly H_2 (160 μL/L). After exposure to H_2, the resistance value becomes smaller, the response value increases and the response is more rapid. The H_2 molecules separate from the material's surface when the target gas in the air cavity is exhausted, which causes the response value to drop quickly and essentially go back to its starting value. The response-recovery times for Pd/C, Pd/C-R and Pd/NC, are approximately 55–57 s, 54–53 s and 52–49 s, respectively. In addition, the Pd/NC material represents a more rapid feedback efficiency from the time point when the response is first triggered, which is necessary for timely monitoring of gas changes.

For the CO test, a more rapid trigger phenomenon is activated for Pd/NC as shown in Figure 4b. A slight merit is presented over the trigger time node of the aforementioned H_2 tests. Once the gas channel was fully established, all the materials responded quickly to CO, generating the response-recovery times for Pd/C, Pd/C-R and Pd/NC of 65–68 s, 62–63 s and 60–56 s, respectively. As can be seen in Figure 4c, the evaluated gas-sensitive materials responded rapidly to 160 μL/L C_2H_2 gas, generating the response-recovery times at 51–53 s, 48–50 s and 47–49 s for Pd/C, Pd/C-R and Pd/NC, respectively.

According to the results of the aforementioned experiments, the cationic Pd/C and Pd/NC samples were better at response recovery than the Pd/C-R sample. The synergistic interaction between the surface nitrogen species and cationic Pd helps to further increase the capacity to respond and recover. Clearly, the cationic Pd and their interaction with N species are the subject of the non-negligible action. Therefore, we are focusing on the mechanism behind this behaviour.

3. Materials and Methods

3.1. Experimental Materials

Ionic liquids (ILs) 1-ethyl-3-methylimidazolium-bis (trifluoromethylsulfonyl) imide [EMIM][NTf_2] and 1-ethyl-3-methylimidazolium dicyanamide [EMIM][$N(CN)_2$], (Lanzhou Greenchem. ILS, LICP. CAS. Lanzhou, China) were mixed together at 50 °C in an aqueous solution of ethanol at a molar ratio of 5:1 [EMIM][NTf_2]:[EMIM][$N(CN)_2$]. The obtained binary IL-mixture was carbonized at 1200 and 600 °C under nitrogen (N_2) atmosphere to synthesize carriers named C, and NC, respectively. Then the Pd/C and Pd/NC samples were prepared using a wet impregnation method. Pd/C was thermally reduced (R) to Pd/C-R catalyst for 120 min at 500 °C amid an atmosphere of hydrogen (H_2). Unless otherwise stated, the notional total metal loading for all the samples was 1 wt.%.

3.2. Materials Characterization and Tests

The AberratioN-C800orrected scanning transmission electron microscopy (AC-STEM) was used for direct analysis of the distribution of isolated single metal atoms. X-ray diffraction (XRD) spectra were recorded on a Panalytical X'Pert PRO instrument with the Cu Kα radiation (λ = 0.15406 nm) at a voltage of 40 kV and a current of 30 mA. The valance state of copper sites was investigated by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Ultra DLD spectrometer. All binding energy values were referenced to the C 1s signal at 284.4 eV. The CGS-8 intelligent analysis system (Beijing Elite Institute, Beijing, China) and an autonomous gas distribution system were combined to create a gas-sensitive test platform in this study for performance testing. The platform is capable of collecting data from 8 channels of gas-sensitive tests, and the operating current of the element may be continually changed by adjusting the heating wire's current in the 0 to 400 mA range. The sensor resistance Rs is from 1 to 500 MΩ.

4. Conclusions

In this work, the effect of distinct Pd/C, Pd/C-R and Pd/NC materials on the gas-sensitive properties was investigated. XRD and XPS characterizations show that the remaining Pd^0 species on carbon were significantly inhibited by the surface N species. Pd/NC explored the superior gas-sensitive performance following the sequence of $H_2 > C_2H_2 > CO$. The synergistic combination between the cationic Pd and the surface nitrogen species activates excellent gas response-recovery capabilities for Pd/NC, indicating the promise of the produced material in gas monitoring. References for gas monitoring of partial discharges in transformers are provided by this research.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13071113/s1, Figure S1: The survey XPS spectra of Pd-C; Table S1: The split peaks processing information of Pd/C; Figure S2: The survey XPS spectra of Pd-NC; Table S2: The split peaks processing information of Pd/NC; Figure S3: The N1s spectrum for Pb/NC.

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