

Powder Microelectrodes Applied to NO_2^- Detection

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Abstract: The reduction of nitrite at Au or carbon electrode in H_2SO_4 was found to follow a chemical-electrochemical (CE) mechanism with a very thin (4×10^{-8} cm) preceding reaction zone. It was proposed and experimentally verified that for such kind of electrode processes the total reaction rate could be effectively enhanced by using electrodes with increased true surface area, such as porous electrodes. As a combination of porous electrode and microelectrode, the powder microelectrode shows excellent performance for nitrite detection.

Keywords: Nitrite reduction; microelectrode; CE mechanism.

The electrochemical behaviors and the detection of NO_2^- have attracted increasing attention recently because of the important roles played by NO_2^- in environment and life processes. Thus, advanced techniques for the determination, especially on-site determination, of the nitrite in foods, biological fluids and environment are highly desired. Compared with other techniques such as spectroscopic and chemical ones, electrochemical methods have the advantages of high sensitivity, quick response, low cost and compatibility with portable instrumentation. Though there have been a number of papers on the electrochemical determination of nitrite¹, none have been universally satisfactory so far. It is still needed to explore new approaches.

The microelectrode technique has been widely used in electrochemical studies and electroanalytical applications owing to a variety of merits. The powder microelectrode (PME) developed in our laboratory is a combination of microelectrode and porous electrode². Besides the many advantages of microelectrodes, the PME has a markedly increased real surface area compared with a smooth electrode and therefore, may provide much higher activity for the heterogeneous reactions taking place at the electrode surface. In this paper we report a new application of the PME and a new approach to accelerate an electrode reaction controlled by a preceding chemical reaction. We will show that when the zone of the preceding reaction is sufficiently thin, the total reaction rate can be increased by using porous electrode and a PME is a handy version for analytical purpose in this case.

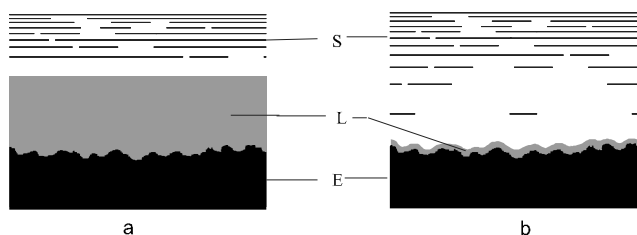
The preparing of PMEs has been detailed elsewhere². A micro-disk electrode made from a Pt wire of 0.1 mm diameter sealed in a glass tubing was etched in aqua regia to form a cavity and then the powder of Au or carbon (acetylene black) was filled in the cavity to form a PME. The real surface areas of the Au and carbon PMEs were estimated

to be about 400 and 1200 times of their apparent area according to the double layer capacitance data. Electrochemical measurements for PME's were carried out with a saturated calomel electrode (SCE) as both the counter and reference electrodes while a Keithley 485 picoammeter was used for current measurements. All solutions were prepared with analytical reagents and doubly distilled water. Acidic solution of NaNO_2 was freshly prepared *prior* to use. The rotating disk electrodes (RDE's) of Au and glassy carbon were also used for mechanistic studies.

It was found that the steady state limiting current I_L for NO_2^- reduction at Au and glassy carbon RDE's in $0.05 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ containing $5 \text{ mmol L}^{-1} \text{ NaNO}_2$ was independent of the rotating rates above 500 rpm and about a hundred times lower than the calculated mass transport limiting current (NO_2^- diffusion coefficient $1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)³. The reaction of NO_2^- reduction was found first order to both NO_2^- and H_3O^+ . These observations indicate that I_L is determined by neither the mass transport nor the electron transfer but by a chemical transformation preceding the electron transfer (the CE mechanism). The preceding reaction is thought to be $\text{HNO}_2 + \text{H}^+ = \text{NO}^+ + \text{H}_2\text{O}$ where the NO^+ is the electroactive species directly accepting electrons from the electrode. According to the theory for the electrode reactions of CE mechanism⁴, the limiting current and the thickness of the preceding reaction zone can be calculated. With the necessary parameter values available in literature³, the calculated I_L was in reasonable agreement with the experimental data, supporting the CE mechanism.

The calculated thickness of the reaction zone turned out to be $\sim 4 \times 10^{-8} \text{ cm}$ that is surprisingly small and comparable to the thickness of the double layer. Therefore the chemical reaction zone in this case should approximately follow the surface morphology of the electrode. Since the total reaction rate is proportional to the area of the reaction zone, the total current of the electrode is expected to be strongly influenced by the roughness of the electrode surface. **Figure 1** illustrates two typical situations regarding relative sizes of the surface roughness and the reaction zone thickness. When the reaction zone is thick compared to the surface roughness (**Figure 1a**), the area of the reaction zone is equal to the apparent area of the electrode and, therefore, the surface roughness has little effect on the apparent current density. In contrast, when the reaction zone is very thin (**Figure 1b**), the area of the reaction zone is larger than the apparent area for roughened electrodes and the apparent current density is increased accordingly. When a porous electrode is used, the gain in total current due to increased surface area should obviously be more prominent.

Figure 1. Schematic presentations showing the relative size of the reaction zone thickness to the surface roughness. a, thick reaction zone; b, thin reaction zone. (E- Electrode substrate; L- Reaction zone; S- bulk solution)



The steady state polarization curves for nitrite reduction at Au and carbon PME are shown in **Figure 2** along with those obtained with Au and glassy carbon RDE's. It is seen that the limiting current densities for NO₂⁻ reduction at Au and carbon PME are about 50 and 100 times larger than that for Au RDE. The current gain for carbon PME is larger than that for the Au PME, apparently in accord with the difference in the real surface areas between the two electrodes. These data strongly support the above discussions based on **Figure 1**. It is interesting that the limiting current for the carbon PME is as large as 169 nA, very close to the diffusion limiting current.

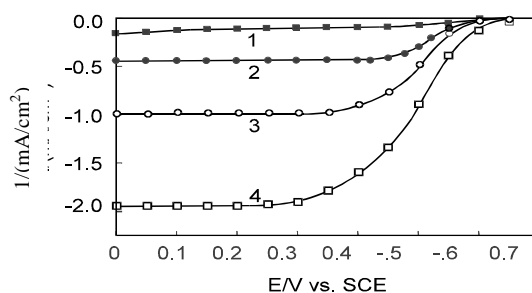
For the CE electrode reactions controlled by a preceding homogeneous chemical reaction, the usual way to accelerate the total reaction rate would be a proper catalyst for the homogeneous reaction. This work proves that if a reaction is controlled by a homogeneous step occurring in a thin region very close to a solid surface, the total reaction may be accelerated by increasing the solid surface area as if the reaction was catalyzed heterogeneously by the solid.

It was also found from **Figure 2** that the plateau of limiting current for the PME is somewhat shorter than that for the RDE's. However, the current plateau is still wide enough for reliable amperometric analyses. A good linearity over 0~0.25 mol L⁻¹ (linear regression coefficient 0.99996) with a high sensitivity 430 mA cm⁻² mol⁻¹ L was obtained for nitrite reduction at carbon PME. These values are better than all reported values except those obtained with an enzyme electrode⁵. However, the PMEs do not have the problem of activity decay often associated with enzymes. The NO₂⁻ detection limit was estimated to be 4.4x10⁻⁶ mol L⁻¹ for signal/noise ratio S/N=4. The 90% response time was about 10 s. Ascorbic acid, Fe³⁺, Fe²⁺, Mg²⁺, Cl⁻, I⁻, NO₃⁻, and PO₄⁻ showed no noticeable interference at concentrations around 0.1 mol L⁻¹. Human saliva samples were tested with the carbon and Au PMEs, giving a result around 1.4x10⁻⁴ mol L⁻¹ that is in reasonable agreement with the literature report⁶. The temperature coefficients of the limiting current, defined as dI/I dT=d(lnI)/dT, for NO₂⁻ reduction at Au and carbon PMEs were 1.4 % / °C and 0.7% / °C in the range 10-65 °C, respectively. These values are markedly lower than the value 3.3% / °C obtained with a smooth Au microelectrode and characteristic of the preceding reaction. Such small temperature coefficients are rarely seen for electrode processes and are advantageous for sensor applications.

The extremely low temperature coefficient and the shortened limiting current plateau for the PMEs may be qualitatively explained in terms of the characteristics of porous electrodes. It is well-known that the current is usually not uniformly distributed along the thickness in a porous electrode (the depth in a PME in this work) owing to the resistivities of mass and charge transports in the porous matrix. In our case, the outer part of the PME is better utilized than the inner part because of the gradual exhausting of the reactants along the depth. This non-uniformity increases with the increasing of the activity per unit volume (the specific activity) of the porous matrix. Any factors causing an increase in the specific activity of the porous matrix would lead to a decrease in the reaction uniformity. Both temperature rising and negative potential shifting increase the specific activity. Because of the increased nonuniformity, the total reactivity of the porous electrode can not increase with temperature as greatly as a smooth electrode made of the same material, resulting in a decreased temperature coefficient. Similarly, the

increment of the total activity of the electrode with the negatively shifting potential is less for the PME than for the smooth electrode. Since the carbon PME has a higher specific activity than the gold PME, the former has an even lower temperature coefficient and larger half wave potential shift to the negative side.

Figure 2. Steady state polarization curves in $0.05 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 5 \times 10^{-3} \text{ mol L}^{-1} \text{ NaNO}_2$. 1, glass carbon RDE (current magnified by 20); 2, Au RDE (current magnified by 20); 3, Au PME; 4, carbon PME.



In summary, this work has proposed and experimentally proved the idea that the apparent limiting current density of EC reactions controlled by the preceding homogeneous chemical reaction can be effectively enhanced by using porous electrodes, if the preceding reaction zone is sufficiently thin. For analytical purposes, the PME is an attractive version of this kind of electrodes. The good performance along with low cost and the ease in preparation and operation makes the PME promising for NO_2^- determination in practice.

Acknowledgment

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