Determination of Proton Diffusion Coefficient in Spherical Nickel Hydroxide Using Potential Step Measurement on Single Beads

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Abstract: The Potential step measurements are carried out on single beads of nickel hydroxide and the results are interpreted with a dual structure model featuring fast and slow diffusing components. The intrinsic diffusion coefficients for the two components are found to be in the order of magnitude 10^{-7} and $10^{-13} \sim 10^{-14}$ $cm^2 s^{-1}$, respectively, with an apparent value for the slow component in the order of $10^{-10} cm^2 s^{-1}$.

Keywords: Nickel hydroxide, proton diffusion, proton vacancy, diffusion coefficient, betteries.

Nickel hydroxide is the active material for the positive electrode of rechargeable alkaline batteries. The proton diffusion in nickel hydroxide is recognized as the rate determining step in charge and discharge of the positive electrode. However, in spite of much work has been done in the past, the problem of diffusion coefficient *(D)* determination cannot be regarded well-solved[1]. The reported experimental *D* values scattered over 6 orders of magnitude, from 10^{-13} to 10^{-7} $cm^2 s^{-1}$. Though the difference in samples and measurement techniques were invoked to explain the discrepancy, problem remains to explain, why the difference in *D* values is so large. Another problem in previous works was the arbitrary assumption of the effective (active) proton concentration. In the present work both the diffusion coefficient and the concentration were determined experimentally and an important new insight is gained into the proton diffusion process in nickel hydroxide.

Experimental

The samples used were single beads of the spherical nickel hydroxide, the currently prevailing form of nickel hydroxide for battery applications. Compared to the works done with practical nickel hydroxide electrodes, the present approach can prevent the influence of the binders and the complexity associated with porous electrodes to obtain the intrinsic parameters of the nickel hydroxide itself. On the other hand, compared to

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Figure 1   Cell design for single bead measurements (the left is enlarged detail)
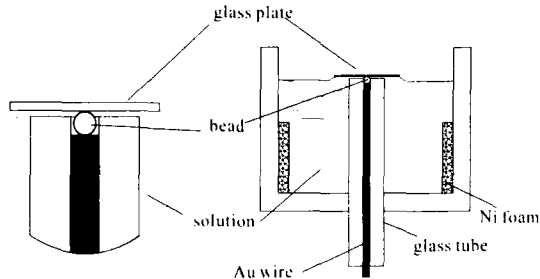
the works with deposited thin films of nickel hydroxide, the spherical diffusion mode in the single bead makes both the diffusion coefficient and the concentration easily accessible (see the Equations 1 and 2 below).

A single bead (20-30 μm in diameter) was held in the cavity at the tip of an Au microelectrode (30 μm diameter), as shown in **Figure 1.** Ni foam served as both the counter and pseudo reference electrodes.   A piece of thin glass was pressed on top of the bead to ensure reliable electrical contact between the bead and the Au surface.   The solution was 6 mol/L KOH and experiments were carried out at room temperature on CHI660 Electroanalyzer (Chenhua, China).   The bead was first held at 1.45 V *(vs.* RHE) for hours to reach full and uniform charge in the whole bead.   The potential was then stepped to 1.15 V and the current response was recorded over 1000 seconds with a sampling frequency of 30 data points per second.

Results and Discussion

The current response of a rechargeable sphere to a potential step is described by a complicated serial function but this function can be simplified for sufficiently short and long time domains.   In these two extremes, the current response can be well described by Equations 1 and 2, respectively[2]:

$$i = 4nF\pi r^2 DC(\frac{1}{\sqrt{\pi Dt}} - \frac{1}{r}) \qquad (1)$$

$$i = (8nF\pi r \cdot DC)exp[(-\pi^2 D/r^2)t] \qquad (2)$$

Note that for simplicity the problem of proton diffusion has been mathematically converted into the problem of proton vacancy diffusion in Equations 1 and 2. C is the concentration of effective (active) proton vacancies in a fully charged sphere; D is the diffusion coefficient of proton vacancies (equal to the diffusion coefficient of protons); r is the radius of the sphere where diffusion takes place; F is the Faraday constant. **Figure 2** prove that the experimental results obeyed the equations to a good approximation.

Uchida and coworkers reported potential step measurements on single beads of nickel hydroxide using a different device[3].   They obtained a plot similar to **Figure** 2B and deduced D to be $3\text{\textasciitilde}4\times10^{9}cm^2s^{-1}$ with an assumed C value.   In contrast to their approach, we deduced both D and C experimentally from the short time (using **Figure**

2A and Equation 1) as well as the long time (using **Figure** 2B and Equation 2) responses, by exploiting both the slope and the intercept of the straight lines shown in **Figures 2A and 2B.**

The data of 12 measurements on 7 beads from two different sources showed the results similar to **Figure 2.** From the initial response current **(Figure 2A)** and Equation 1 with the bead radius taken for r, D values ranging $1\text{-}3\times10^{-7}$ cm^2s^{-1} were obtained. On the other hand, from the long term response **(Figure 2B)** and Equation 2 with the same r value, much smaller D values ranging $2\text{-}9\times10^{-9}$ cm^2s^{-1} were obtained. It is noteworthy that the diffusion coefficients deduced from the two time domains differed by about three orders of magnitude. The C values obtained from the two time domains were in the same order of magnitude but differed by a factor ranging 1.3-3.1. However, it is very interesting that the sum of the two concentration values turned out to be approximately (within about 10%) equal to the concentration of effective proton vacancies converted from the measured discharge capacities of the beads.

These results can be interpreted with a dual structure model featuring two kinds of effective proton vacancies associated with large and small D values, respectively. In the model, the slow diffusing component is the solid grains (crystalline) with diameters below 0.1 μm while the fast diffusing component is a matrix composed of nano particles. In a bead of spherical nickel hydroxide the fast component forms a continuous phase which is slightly water permeable and the solid grains are densely packed in the matrix. The suggested dual structure is supported by preliminary results of atomic force microscopy (AFM) observations and water absorption measurements. **Figure 3** is an AFM image showing the morphology of the cross section of a single bead nickel hydroxide. The sub-micron grains are visible in the AFM image, in support of our assumptions.

According to the dual structure model, the initial current response in potential step measurements is dominated by the proton diffusion in the fast component in the radial direction of the bead. In the later period (the long time domain), the fast component has been exhausted and the current is governed by the diffusion within the grains **(Figure 2B).** Therefore, when Equation 2 is used to describe **Figure** 2B, the radius of the grain

Figure 2 Transient current responses of a single spherical bead $(r = 12.5$ μm$)$
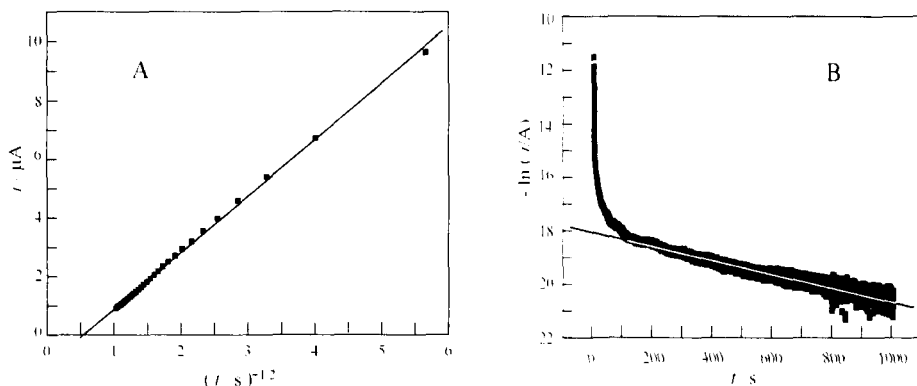
(A) The first second and (B) over 1000 seconds.

Figure 3   AFM image of a cross section of single bead nickel hydroxide (area 1 μm × 1 μm)

instead of the radius of the single bead should be taken for *r*.   The *D* thus obtained was in the range 10^{-13}-10^{-14} cm^{2}s^{-1}, comparable to the lower limit of the *D* values found in literature.

According to the dual structure model, the upper limit value round 10^{-7} cm^{2}s^{-1} is characteristic of the fast component which can be obtained only from the samples with thickness (for films) or radius (for spheres) larger than the grain size by orders of magnitude otherwise the time interval of the plot in **Figure 2A** would be too short to be useful.   For these thick samples, when the long term response **(Figure 2B)** is used and the bead radius is taken (mistakenly) for the *r* in Equation 2 to deduce *D* for the slow component, a value larger several orders of magnitude (depending on actual thickness or radius) than the intrinsic value will result, usually in the range 10^{-9}-10^{-11} cm^{2}s^{-1}. Obviously, the *D* values thus obtained are apparent values *per se*. *I*n contrast, for samples with thickness or radius comparable with the grain size, the deduced *D* would be close to that intrinsic for the grains.   These predictions are in reasonable agreement with literature reports and, therefore, the unusually large discrepancy over the *D* values can be understood based on the dual structure model. In contrast to the approach prevailing in literature, our new findings indicate the necessity to consider the inhomogeneity in nickel hydroxides when proton diffusion is in concern.

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