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Preparation and Performance Evaluation of Zn Electrode in Zn-Ag Battery

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With the development of space science and the military, the use of high-current power supply devices has attracted much attention. Zinc-silver primary batteries have the advantages of high specific energy density, stable working voltage, high charging efficiency, safety, and environmental friendliness, zinc-silver primary batteries have proven to be a source of high power. The Zn electrode in battery still faces some serious challenges, such as nonporous, uneven surface, and unendurable. In recent years, some attempts have been to increase the performance of Zn-Ag batteries by increasing the porosity and durability of the electrode by using flexible conductivity adhesives. In this work, we used nanofiber polymer glue as the material adhesive in the electrode. Here aramid nanofibers (ANFs) are used to bond zinc particles on the collector. The mixture of ANFs and Zn powders was coated on the copper mesh and compressed under 1 MPa pressure after drying at 150□C for 4 hrs. SEM images investigated the morphology of the Zn electrode with the distribution of Zn particles and ANFs on the surface electrode. The electrochemical performance such as the current and potential of the Zn-Ag battery was evaluated and obtained the maximum value 3.7A with 2%wt. ANFs in the mixture.

Keywords: ANFs; material adhesive; porosity; zinc-silver battery

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The alkaline battery was first invented by Lewis Frederick Urry, a Canadian-American chemical engineer, and inventor, due to many factors affecting and requiring batteries, new inventions and systems of alkaline batteries were born [1]. Compared to other battery types, alkaline batteries have a higher energy density, which contributes to narrowing the gap between lithium-ion batteries (LIB) and supercapacitors (SC) [2]. However, each type of alkaline battery developed in each period has different disadvantages, the biggest weakness of alkaline batteries is the low energy supply capacity. The alkaline silver-zinc battery system has indeed been the subject of numerous studies due to its high energy density and efficiency. The silver battery system was first practically developed by Michel Yardney [3] and Professor Henri Andre more than 60 years ago [4]. Zinc-Silver (Zn-Ag) electrochemical systems have been used for a long time, in the form of primary power sources (batteries) and secondary power sources (batteries). Since then, the primary and secondary Zn-Ag battery systems have attracted many different applications because they possess high security, reliability, and safety, as well as the highest output work per unit mass and volume. Zn-Ag batteries have been widely utilized for an extended period for watches, hearing aids, military, and aerospace. Compared with other conventional power sources, Zn-Ag batteries have superior features such as specific energy, and specific capacity, allowing discharge with large current intensity and stable working voltage output. Therefore, these advantages reimburse for the limitations of the high cost of silver [5]. In addition, Zn-Ag batteries are inherently safe due to the use of aqueous electrolytes, which can avoid flammability problems [6]. Another superlative feature of using Zn-Ag batteries, which are made of non-toxic elements, also contributes to environmental friendliness [7]. Despite their excellent features, Zn-Ag batteries share common disadvantages with other battery types, particularly primary Zn-Ag batteries, which deliver high current, are disposable, and are typically used in specialized applications. The inherent issue correlated to Zn anode is the well-known porosity based on binders.

Many colloidal systems have been applied as binders for materials in electrodes such as polyvinyl alcohol (PVA), polytetrafluoroethylen (PTFE), polyvinylidene fluoride (PVDF) and derivative binders represented by carboxymethyl cellulose (CMC). Kumar et. [8] fabricated Zn electrodes with a 5 wt.% PEO binder for Zn-Ag_2O batteries with stable operating voltages (>1.4 V) at high current densities (1–12 mA cm^{-2}) and achieved the highest areal capacity reported for fully printed batteries at 11 mAh cm^{-2}. Gizem and Ozgenc [9], fabricated Zn electrodes for Ni-Zn batteries with 6 wt.% PVA and 3 wt.% PEG providing

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discharge capacities of 157 mAh g^{-1} and 311 mAh g^{-1}, respectively. Another work was reported by Akash Kota et al. [10] fabricated primary Ag_2O–Zn cells, Zn electrode with 5 wt.% PVDF was fabricated by stencil printing method. However, many adhesive systems used in electrode applications are mechanically unstable, exhibit limited porosity, and demonstrate poor ionic conductivity, complicating their use in primary batteries that require high currents over short durations.

Polymer nanofibers, especially aramid nanofibers (ANFs) possess properties such as high porosity, large specific surface area, high aspect ratio, low density, and unique nano-effect, which have been attracted the attention and applied in many fields [11]. Furthermore, ANF-based materials have been functionalized to fabricate conductive fibers and hydrophobic textiles [12]. Besides, ANFs are well-known as highly wettable materials and are commonly used in battery separators [13]. The combination of materials electrode and ANFs enhances the wettability between the electrode and electrolytes, improving ionic conductivity [14]. Moreover, the research on the use of ANFs as a binder material in the electrode in silver-zinc batteries has been disregarded.

In this work, the Zn electrode was fabricated with the combination of ANFs binder system to solve the porosity problem. The charge transfer ability of Zn electrode has been improved with the high current to response the requirements for disposable Zn-Ag batteries. Specifically, the effect of ANFs binder wt.%, carbon black, KOH concentration and drying temperature has been evaluated to find the optimal condition of the battery based on the current intensity.

EXPERIMENTAL

Chemical and Material

Materials: Zinc powder (Zn) (≥90%) was provided from Xilong Scientific Co., Ltd, China. Potassium hydroxide (KOH) (≥85%); and dimethylsulfoxide (DMSO) (>99.8%, GC) were obtained from Guangdong Guanghua Sci-Tech Co., Ltd, China. Kevlar fiber was purchased from DuPont Ltd., Wilmington, DE, USA. Cellulose separator commercial was purchased from XNK Co., Ltd, Vietnam; carbon black was sourced from Shantou Xilong Chemical Factory Co., Ltd, China.

Procedure

ANFs solution: The mixture of 100 mL dimethyl sulfoxide (DMSO) and 0.75g KOH was prepared on the neutral flask to combine with the addition of some water droplets. After, poly-para phenylene terephthalate (PPTA) fibers were cut into small-sized fibers and put into an above mixture. Then, the mixture was stirred for 7 days to obtain a 10 mg mL^{-1} ANFs solution.

Preparation of Zinc electrodes: The commercial zinc powder is milled by a Zirconia ball for 4 hrs at room temperature and sieved by a 125 μm mesh to remove the large particles. After sieving, zinc powder is mixed with ANF solution and carbon black (CB) active material with different ratios. The mixture is stirred for 6 hours to achieve homogeneity. The homogeneous mixture was coated on copper mesh and was compressed with 1 MPa. Then, the electrodes were dried in a vacuum oven at different temperatures for 4 hours. The electrical properties and impedance performance of fabricated zinc electrodes were investigated with the combination of the commercial silver electrodes in the Zn-Ag battery.

Characterization Methods

Material characterization: FT-IR spectrum of the electrode material was recorded using a Varian FTS 2000 spectrometer. The morphology and the element contents of the fabricated Zn electrode were measured using a field emission scanning electron microscope (FESEM) (Hitachi FE-SEM). The X-ray diffraction pattern of the polarized material was recorded on a Malvern Panalytical Diffractometer with an X-ray tube made of Cu (Cu-Kα, λ=0.15418nm). Diffraction angle from 20 to 90°, scanning step 0.02° scanning speed 0.2° $seconds^{-1}$.

Electrical and electrochemical measurement: The current and voltage values of the Silver-Zinc battery were evaluated by VOC ΛNENG®DT9205A. The Zn-Ag battery was prepared in a size of 4cmx4cm and dipped in KOH solution as the electrolyte with concentrations. Electrochemical impedance spectroscopy (EIS) was evaluated by the two-electrode method using (Bio-Logic SAS; Model: SP-150e) to investigate the resistance of the charge transfer process. The coating Zn paste was dropped on surface of the two Electrode Swagelok Cell.

RESULTS AND DISCUSSION

The anode electrode was prepared by Zn powder with 2 wt.% ANFs binder and 1 wt.% carbon black as the conductive material to characterized the properties by using FT-IR spectrum, XRD pattern, SEM images, and EDX spectrum. The FT-IR results of Zn anode material are measured and shown in **Figure 1(a)**. The FT-IR spectrum analysis results of the material show the absorption band of the characteristic N-H functional group vibrations at peaks 1645.19 cm^{-1} and 823.79 (cm^{-1}) to demonstrate the presence of amine group (ANFs) in the anode structure [15]. Additionally, the using carbon black in anode was confirmed by the absorption peaks at 1538.78 cm^{-1} and 1511.81 cm^{-1} of the characteristic C=C functional group vibrations [16]. The formation of ZnO from Zn powder due to the surface oxidation in the dry process at high temperatures (150 °C) is demonstrated by the characteristic Zn-O functional group vibrations at peaks 1630 cm^{-1} [17] and 1030 cm^{-1} [18].

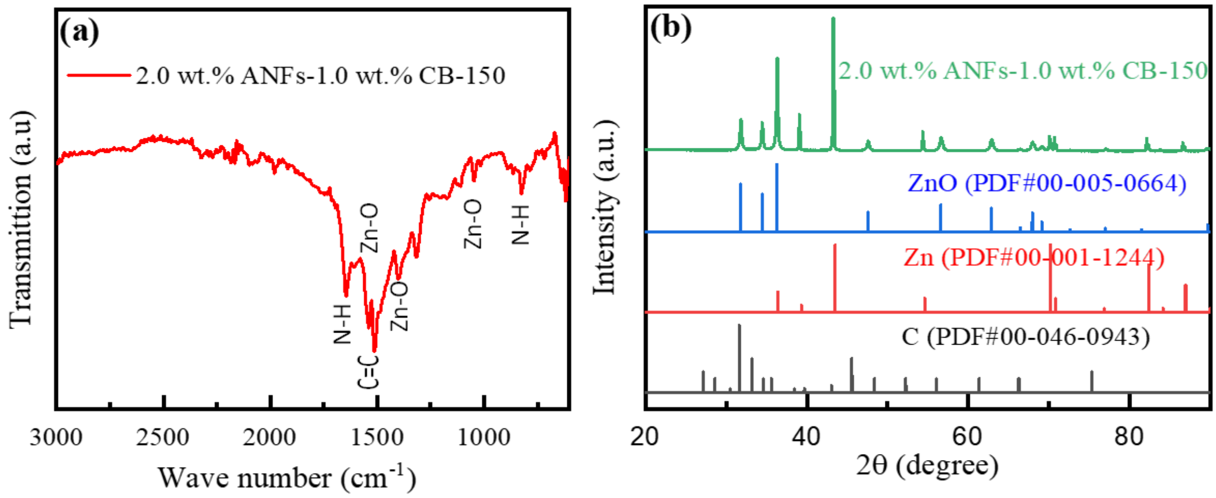

Figure 1. (a) FT-IR spectra result of the zinc electrode; (b) XRD spectra of the zinc electrode.

The X-ray diffraction pattern of the anode electrode material is shown in **Figure 1(b)**. The result confirmed the appearance of Zn and ZnO in the anode structure by the comparison with the standard spectrum Zn (PDF#00-001-1244) with the typical peaks of (002) and (101) at 36.3 and 43.4 degrees, respectively and the of ZnO (PDF#00-005-0664) with typical peaks of (100) and (101) at 31.8 and 36.3 degrees, respectively. However, the characteristic peak of carbon materials cannot be detected due to the atmosphere structure of the commercial carbon black.

The results of the surface morphology analysis of the electrode were observed by SEM images with 2000x magnification (**Figure 2(a)**). Commercial zinc particles have no uniform size and are clumpy, which prevents a homogeneity of the coating mixture of zinc powders, ANF binder, and carbon black. Therefore, commercial Zn powder needs to be pretreated before blending with ANFs and carbon. The milling by zirconia ball for 4 hrs and the sieving process by a sieve with a mesh size of 125 µm to remove the large size of Zn particles. From the SEM image in **Figure 2(a)**, the Zn particles with a size from 10 to 2.5 µm. In addition, a dark coating in the SEM image is believed to be the coating of ANF binder. This coating does not completely cover the surface of zinc particles due to the controlled amount (2 wt.%) during the mixing process. Moreover, the use of a small amount of ANFs also ensures the conductivity of the electrode during the electrochemical process. At 10000x magnification, a small amount of carbon appears on the surface of the zinc particles to support the conductivity of the anode electrode as shown in **Figure 2(b)**.

The element contents of the electrode surface are analyzed by EDX spectroscopy as shown in **Figure 2(c)**. The presence of Zn, N, O, and C elements in the EDX result demonstrates the distribution of all materials on the electrode surface. Besides, the high contents of C element are explained by the fact that carbon has a smaller size and density than zinc to conduct the easy appearance of carbon black on the electrode surface. Besides, the percentage of O atoms is also relatively high due to the oxidation of Zn powder during the drying process at high temperatures.

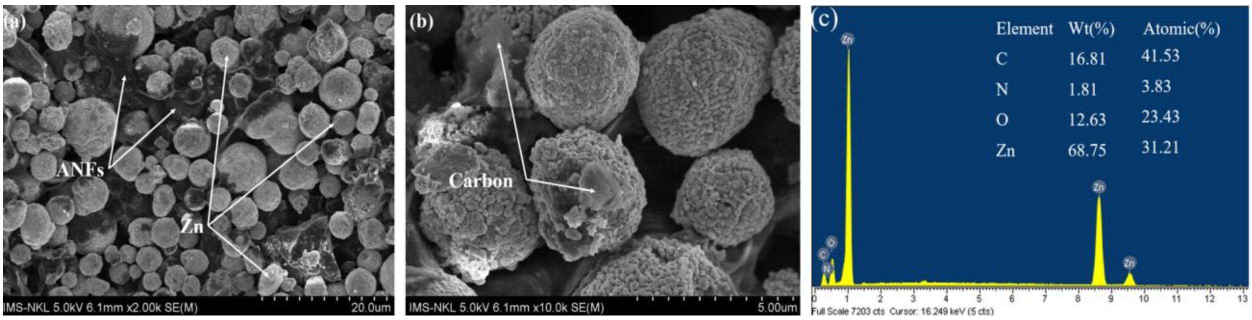

Figure 2. (a) Morphology evolution of zinc electrodes at magnification 20.0 µm; (b) Morphology evolution of zinc electrodes at magnification 5.0 µm; (c) EDX spectra of zinc electrode.

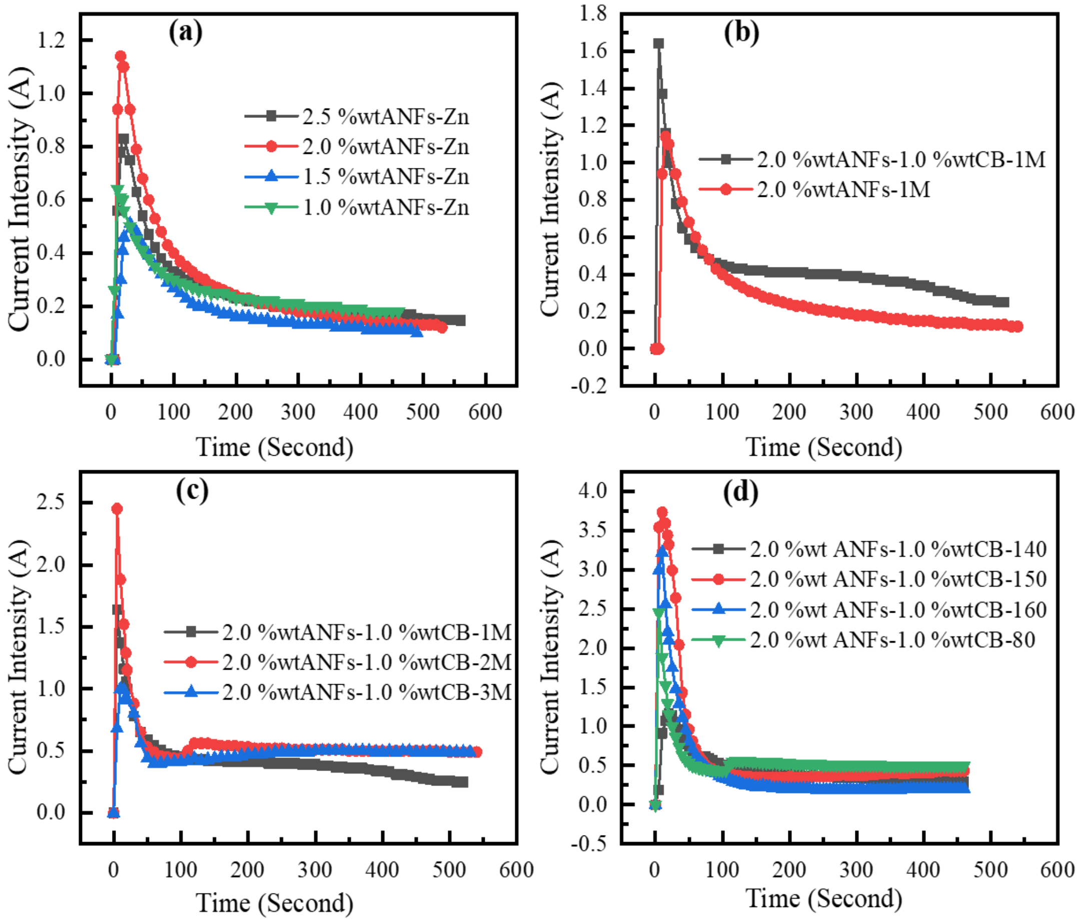

Figure 3. Results of surveys of current intensity characteristics of the electrode (a) Investigation of the influence of binder content; (b) Investigation of the influence of active additive content; (c) Investigation of the effect of KOH concentration; (d) Investigation of the effect of drying temperature.

Electrochemical Performance of the Zinc Electrode

The electrochemical performance of the anode electrode is tested based on the battery structure with cellulose paper as separator and liquid KOH electrolyte at room temperature and atmosphere pressure conditions. The anode electrode is fabricated with different conditions such as content of ANFs, carbon black, concentration of KOH electrode, and drying temperature as shown in **Figure 3**. The result of the current intensity investigation in Zn-Ag battery versus time is calculated from the beginning of the addition of KOH electrolyte (**Figure 3(a)**) with the same of Ag electrode between the samples. In **Figure 3(a)**, the binder ANFs were investigated gradually the increase of the content from 1 to 2.5 wt.%. In the same measurement condition, the current intensity increased gradually with increasing ANF content (from 1 to 2 wt.%) and decreased with increasing ANF content to 2.5 wt.%. The difference in the current intensity value can be predicted that the ANF content is higher than 2 wt.% conduct to the dense cover of ANFs on the surface Zn particles and reduces the conductivity of the electrode (increase resistance). With the lower ANF content, the permeability of the electrolyte solution into the inside electrode. Moreover, the lower ANF content also reduces the adhesion of the electrode, leading to the disintegration of the material when the electrolyte is added. Thus, the electrode can obtain high current values of 2 wt.% ANFs. EIS measurement of the 1.5 and 2 wt.% ANFs samples were also investigated to confirm the current intensity as shown in **Figure 4(a)**. From the EIS result, the resistance of the charge transfer process is calculated by the fitting EIS result through the equivalent circuit and obtaining 4910.89Ω with 1.5 wt.% and 1295.19Ω with 2 wt.%. In the structure of ANFs, the N-H functional groups with high wettability are supported for the charge transfer in the electrochemical process of the Zn-Ag battery.

In **Figure 3(b)**, the comparison between with and without carbon black (1 wt.%) in the Zn electrode is investigated. The current intensity increases from 1.2 to 1.6 A with the presence of C to enhance the conductivity of the anode electrode. The concentration of KOH electrolyte solution is one of the factors affecting the electrochemical properties of the anode electrode. The results of the current intensity according to the electrolyte concentration were studied with the increase of KOH electrolyte from 1 to 3M as shown in **Figure 3(c)**. In batteries, the electrochemical performance depends on the concentration of electrolyte. However, the high KOH concentrations also prevent the charge transfer process due to the increased viscosity of electrolytes with increasing KOH concentration. The high viscosity has reduced the mobility of charge carriers during the electrochemical process. In the study of Arias et al., it was also shown that for silver-zinc batteries, adjusting the KOH concentration in the electrolyte. The electrolyte concentration (2M) could improve the long-term stability of zinc-silver batteries [19]. The results of the current intensity are confirmed by EIS measurement with the concentration 1M and 2M of KOH (as shown in **Figure 4(b)**). The charge transfer resistance obtained 1102.046Ω with 1M and 80.01Ω with 2 M of KOH electrolyte to demonstrate the electrochemical ability of the high concentration electrolyte.

Finally, the Zn electrode is studied for the influence of the drying temperature on the current density. With the sample dried at 80 °C, the current intensity value is lower than that required by a commercial Zn-Ag cell. At 80 °C, the expansion between the ANF binder material is too small, leading to a low porosity density of the electrode structure. Therefore, the charge carriers in the KOH electrolyte solution are difficult to rapidly penetrate the electrode, resulting in the current intensity not responding to the requirements of a Zn-Ag battery. With samples dried at high temperatures from 140 to 160 °C, the current intensity obtained has a large change in value. The best current intensity is achieved at 150 °C and meets the requirements of commercial batteries. A comparison of the current densities corresponding to the commercial battery and the sample, dried at 150 °C, is shown in **Table 1**. With increasing temperature, the evaporation of DMSO and the solidification rate of the electrode occur faster, making the structure more porous [20,21]. However, the high temperature (160 °C) leads to difficulty in controlling the evaporation rate and solidification, making to shrinkage and the crack in the electrode structure.

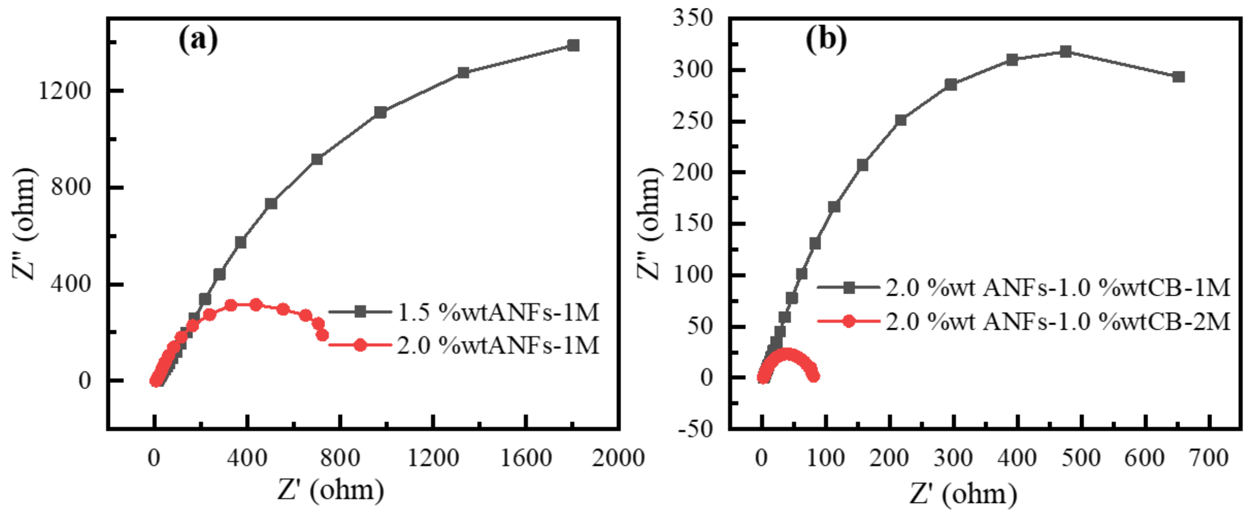

Figure 4. Electrochemical impedance spectroscopy (Nyquist plot) results of sample highest and lowest (a) Investigation of the influence of binder content; (b) Investigation of the effect of KOH concentration

Table 1. The electrical parameter comparison of Zn-Ag batteries.

Parameters	**Commercial battery**	**Experimental battery**
Current density (A cm^{-2})	0.212	0.2375
Voltage (V)	1.6	1.6

CONCLUSION

In this study, the use of ANFs in the battery structure gives a higher advantage for Zn-Ag batteries. ANF binder in DMSO solvent can withstand high temperatures and high adhesion for Zn particles. The properties of the Zn electrode were investigated under different conditions such as ANF content, KOH concentration, and drying temperature. The electrode material is optimized with 2 wt.% binder, a carbon black content of 1 wt.%, dried at 150 °C, and operated in a 2M KOH electrolyte solution. This research battery with the combination of ANF binder and carbon black has a higher current density than commercial batteries with the same voltage.

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