Fabrication and Characterization of Electrospun Sulfonated Poly(phthalazinone ether ketone) Mats as Potential Matrix of Reinforced Proton Exchange Membranes

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ABSTRACT: In this paper, the sulfonated poly(phthalazinone ether ketone) (SPPEK) nanofibers with low sulfonation degree are fabricated by electrospinning for the first time. The optimized concentration of SPPEK for electrospinning is 0.16 g ml^{-1} and the suitable solvent is the mixture of DMAc and NMP. The resulting SPPEK nanofibers show smooth surfaces and uniform diameters of about 50 nm. Proton conductivities of the SPPEK mat and membrane are tested and compared. The result indicates that the proton conductivity of the SPPEK mat is almost five times as high as that of the SPPEK membrane because of the formation of long-range proton pathways on the surfaces of SPPEK nanofibers. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4581–4586, 2013

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are commonly considered as one of the promising alternative power sources because of their high efficiency and environmental compatibility. Proton exchange membranes (PEMs) are the key components in PEMFCs, and the commonly used PEMs are Nafion membranes because of their excellent proton conductivity, good oxidative and chemical stabilities. However, the drawbacks of Nafion, such as high production cost, low thermal stability, and high fuel permeability, obstruct the widespread commercial applications of PEMFCs.[1]

To solve these problems, efforts have been made to develop alternative PEMs. One solution is to develop novel alternative PEMs based on the sulfonated aromatic hydrocarbon polymers, such as sulfonated poly(arylene ether sulfone)s,[2–5] sulfonated poly(arylene ether ketone)s,[6,7] sulfonated polyimides,[8–10] and sulfonated organic–inorganic hybrids.[11–13] The other is to modify Nafion membrane, including the reinforcement of Nafion membrane with a supporting porous substrate,[14–16] the incorporation of inorganic fillers[17,18] and the forming of methanol-blocking layer.[19–21]

The reinforcement of Nafion membrane is an efficient method, which can prepare ultrathin reinforced Nafion membrane because of supporting porous substrates with high strength. Electrospinning is capable of producing nanofibrous polymeric mats, which can be used in many fields.[16,22–24] For example, Nanocomposite membranes made up of Nafion and electrospun polyvinyl alcohol suggested that significant savings in the consumed amount of Nafion could be afforded while keeping high performances.[16]

In our work, we presented a first time fabrication of electrospun sulfonated poly(phthalazinone ether ketone) (SPPEK) nanofiber mats, then employed the FT-IR spectrum and scanning electron microscope (SEM) to character them. Furthermore, proton conductivities of the SPPEK mat and membrane were tested and compared.

EXPERIMENTAL

Materials
The properties of chemicals are listed in Table I.

Sulfonation of PPEK
After being dried at 105°C for 4 h, 5 g PPEK powder was dissolved in 50 mL concentrated sulfuric acid of 98% under an argon atmosphere and the mixture was heated to 80°C. Then 5 mL of chlorosulfonic acid (0.075 mol) dissolved in 30 mL of 98% concentrated sulfuric acid was added dropwise at the same

Table I. The Properties of Chemicals

Chemical	Grade	Manufacturer	Roles of chemical
Poly(phthalazinone ether ketone) (PPEK)	Industrial grade	Dalian Polymer New Material, China	Powdery, starting material
Chlorosulfonic acid	Industrial grade	Shanghai Wujing Chemical, China	Sulfonating agent for PEEK
Concentrated sulfuric acid	Industrial grade	Guangzhou Chemical Reagent Second Factory, China	Solvent for PEEK
N,N-Dimethyl acetamide (DMAc)	Analytical reagent	Tianjin Damao Chemical Reagent factory	Solvent for SPEEK
N-Methyl-2-pyrrolidone (NMP)	Analytical reagent	Tianjin Damao Chemical Reagent factory	Solvent for SPEEK

temperature and the reaction mixture was vigorously stirred for 2 h. Then the reaction mixture was poured onto crushed ice, and the resulting precipitate was recovered by filtration, washed with deionized water until pH 6–7 and kept in a oven at 80°C for 24 h in turn. The sulfonation degree of SPPEK is about 0.64.

Preparation of SPPEK membrane
The SPPEK membrane was prepared by solution casting from solution of the acid form of SPPEK. The SPPEK solution of DMAc (0.20 g mL^{-1}) was stirred for 16 h at 50°C. Then, the solution was spread on a glass plate with a glass knife. The film was dried under ambient conditions for 3 days and then under vacuum at 80°C for 24 h and 120°C for 24 h. The resulting SPPEK membrane was transparent with a yellow color.

Electrospinning of SPPEK Mats
The SPPEK mats were fabricated using an electrospinning apparatus (see Supporting Information Figure 2). The typical electrospinning parameters were as follows: The SPPEK solution with a concentration of 0.22, 0.18, 0.16, or 0.14 g mL^{-1} was prepared by dissolving SPPEK in solvent (DMAc, NMP, or their mixture). The prepared SPPEK solutions was first loaded into a plastic syringe with a needle of ø = 6 mm. A constant volume of the solution was delivered to the needle at a flow rate of 0.40 mL h^{-1}. A distance of 16 cm was kept between the syringe tip and collector (stannum foil). A potential difference of 30 kV was kept between the needle of the syringe and the collector at 40°C and relative humidity (RH) of 40%. The nonwoven fiber mats were collected on the stannum foil connected to the ground.

The SPPEK and phosphotungstic acid (PWA) composite nanofibers were produced through the same procedure. The content of PWA in SPPEK and PWA was 10 wt %, and the concentration of the SPPEK and PWA mixture (NMP as solvent) is 0.16 g mL^{-1}.

Characterization
The FT-IR spectrum was recorded on Nicolet5700 pectrometer. The morphologies of the SPPEK mats and membrane were sputtered with gold and determined by using JSM-6330F SEM and the surface mapping by EDX spectroscopy.

Proton conductivities (σ) of the SPPEK membrane and mat were measured by two-probe AC method from 1 Hz to 500 kHz and 10 mV AC perturbation on a multichannel potentiostat (Bio-logic VMP3, France). A sample with a size of 10 mm × 10 mm was placed in an open, temperature controlled cell where it was clamped between two blocking gilded stainless steel electrodes. Specimens were soaked in deionized water prior to the test. The impedance measurements were performed in water with 100% RH at desired temperature. The σ of the membranes in the transverse direction was calculated from the impedance data, using the formula:

$$\sigma = \frac{d}{R \cdot A} \qquad (1)$$

where d and A are the thickness and face area of the sample, respectively, and R is derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Z axis.

RESULTS AND DISCUSSION

FT-IR and SEM Characterization
The FT-IR and EDX mapping analysis indicates that the PEEK has been successfully sulphonated (see Supporting Information).

Electrospinning is a facile and versatile means for the fabrication of ultrathin fibers from plenty of polymers. It is well known that the shapes of electrospun fibers are significantly affected by the electrospinning parameters, such as entanglements of polymer chains, viscosity and feed rate of the polymer solution, polarity and surface tension of the solvents, applied voltage and the distance between the spinneret and the collector. The SEM images of the electrospun SPPEK fibers from different concentrations are shown in Figure 1. It can be found that significant morphological changes of the resulted SPPEK fibers occur when the concentration (or viscosity) of the polymer solution is changed. Figure 1(a,b) shows the morphology of fibers formed by 0.22 g mL^{-1} solutions using DMAc and NMP as solvent, respectively. Both of them have diameters higher than 1 μm and coarse surfaces because of their high solution concentration or viscosity. When the concentrations are decreased to 0.18 g mL^{-1}, only fibers with defect and diverse diameters are produced [Figure 1(c,d)]. With further reduction of the solution concentrations (0.16 g mL^{-1}), fibers with less defect and rather thin diameters are fabricated [Figure 1(e,f)]. However, the electrospun nanofibers are composed of fibers and beads at solution concentrations of 0.14 g mL^{-1} [Figure 1(e,f)] because the electrostatic forces do not prevent the solution jet
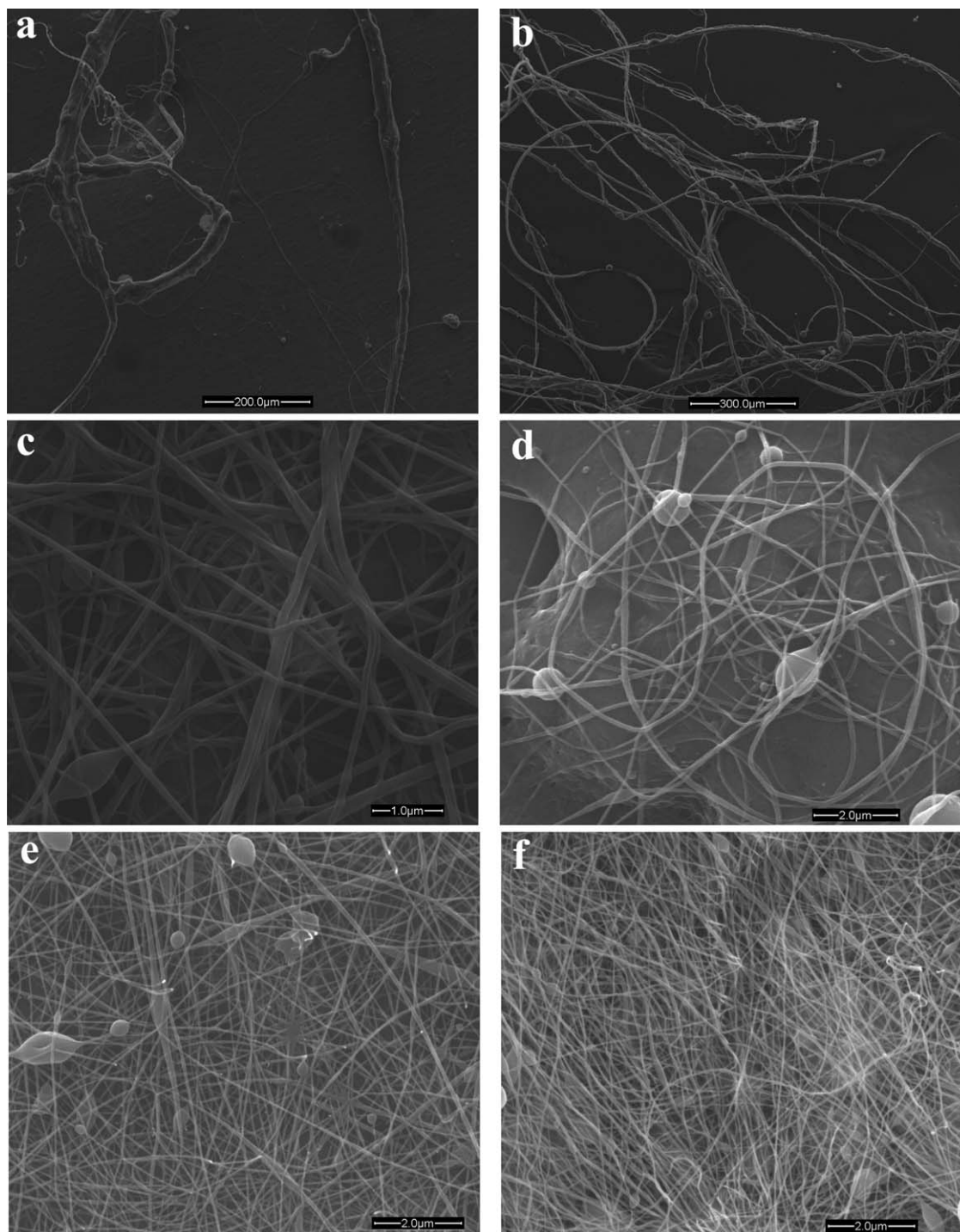
Figure 1. The SEM images of electrospun SPPEK fibers from different concentrations. (a, c, e, g) using DMAc as solvent, the concentrations were 0.22, 0.18, 0.16, and 0.14 g mL^{-1}, respectively. (b, d, f, h) using NMP as solvent, the concentrations were 0.22, 0.18, 0.16, and 0.14 g mL^{-1}, respectively. (i) Using mixture of 20 vol % DMAc and 80 vol % NMP as solvent, the concentration was 0.16 g mL^{-1}. (j) Using mixture of 50 vol % DMAc and 50 vol % NMP as solvent, the concentration was 0.16 g mL^{-1}.

from separating into droplets because of the surface tension of the solution.

For the sake of preparing ultrafine and defect-free fibers, the mixture of DMAc and NMP are employed as solvent. Just as shown in Figure 1(i,j), these fibers have uniform diameters of

about 50 nm and smooth surfaces, probably as the electrospinning conditions may well balance the relations among the solution viscosity, solution surface tension, and electrostatic forces.

It has been demonstrated that the homogeneous composite membrane based on SPPEK and PWA could be prepared by dissolving
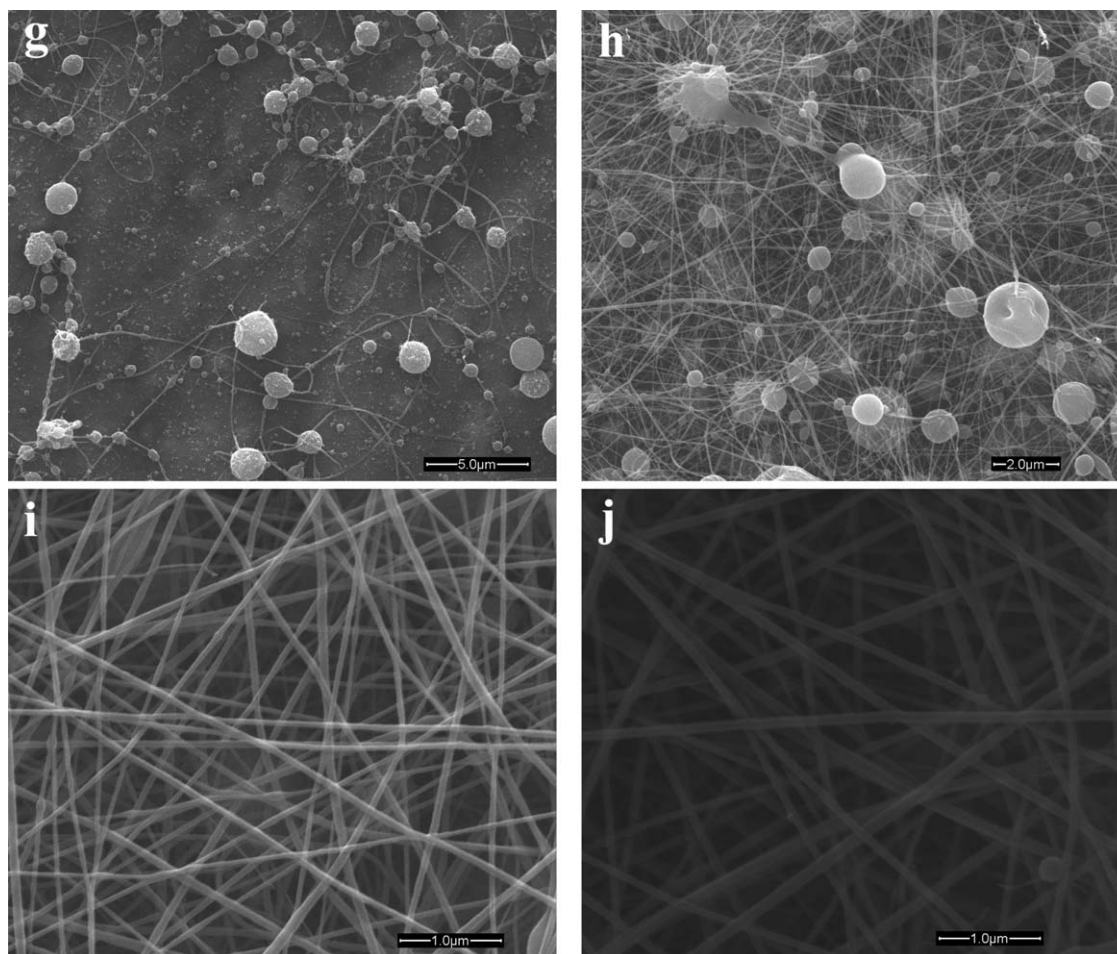
Figure 1. (*Continued*).

them in NMP and displayed better performance than plain SPPEK membrane.[25] The composite fibers from SPPEK and PWA are also fabricated, but it is impossible to produce continuous nanofibers at a concentration of 0.16 g mL^{-1} (Figure 2).

Proton Conductivity

The proton conductivities of the SPPEK membrane and mat are determined at different temperatures by ac impedance spectros-

copy (Figure 3). Although they have the same degree of sulfonation, the SPPEK membrane and mat show obviously different trends. Firstly, the proton conductivities of the SPPEK mat increase with the increase of the temperature because the increase in temperature is favored for fast proton conductivity. Furthermore, the proton conductivity of the SPPEK mat still increases up to 1.3×10^{-3} S/cm at the temperature higher than 80°C because the existence of long-range proton pathways in
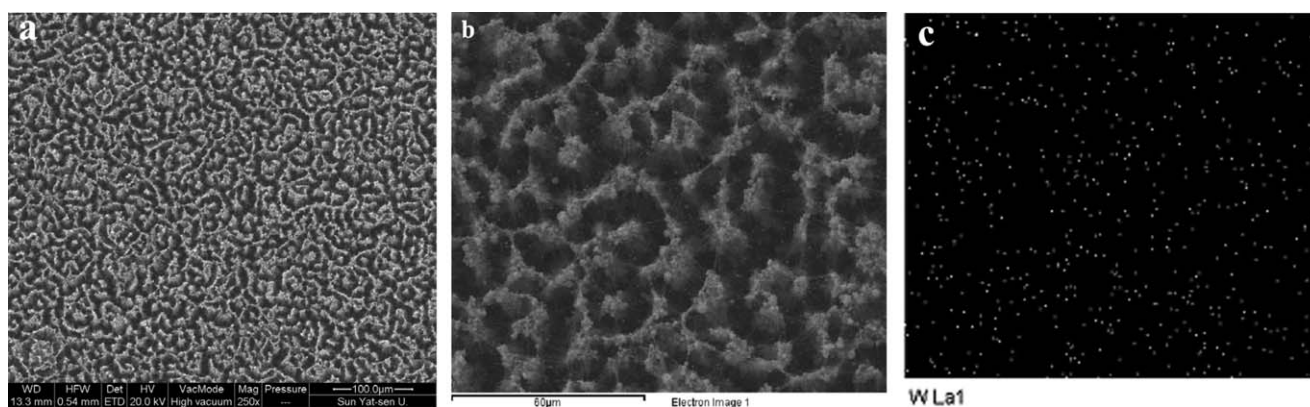

Figure 2. The SEM micrograph (a,b) and EDX dot mapping image for tungsten element (c) of the SPPEK and PWA composite fibers.
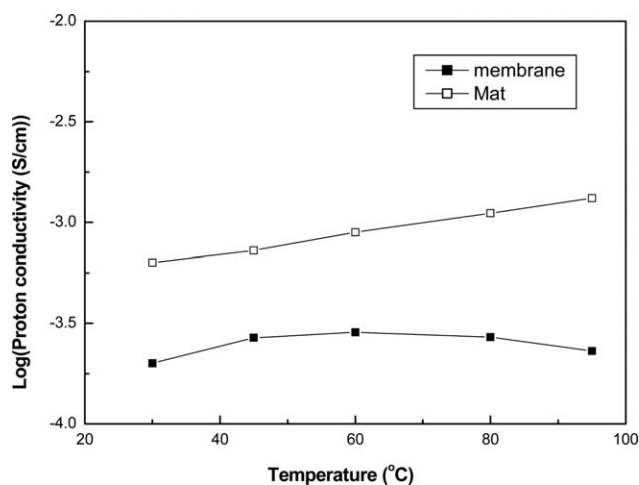
Figure 3. Proton conductivities of the SPPEK membrane and mat.

SPPEK mats overwhelms the negative impact of water loss. But the proton conductivities of the SPPEK membrane display a peak value at 80°C and slight decrease at 95°C because of water loss. Secondly, the proton conductivity of SPPEK mat is nearly five times as high as that of SPPEK membrane. The result is consonant with Refs. 26,27. For the phenomena, the two reports present different explanations, although both of them thought that there are long-range proton pathways formed during electrospinning process. One thought the long-range proton pathways are formed in nanofibers,[26] while the other thought the long-range proton pathways are formed on the surfaces of nanofibers.[27] We are agreed with the latter explanation [Figure 4(b)] because the former [Figure 4(a)] is unfavorable to proton transfer between nanofibers.

CONCLUSION

Uniform nonbeaded SPPEK nanofibers with smooth surfaces and uniform diameters of about 50 nm are fabricated by electrospinning. The optimized concentration of SPPEK for electrospinning is 0.16 g mL^{-1} and the suitable solvent is the mixture of DMAc and NMP. It is considered that the ionic clusters are enriched on the surfaces of nanofibers and that the protons are rapidly and efficiently transported in the SPPEK nanofibers, which leads to the enhancement of the conductivity. As a consequence, the SPPEK mat displays enhanced proton conductivities, which are five times higher than that of the SPPEK casting membrane.

As the SPPEK nanofibers are hydrophilic, it is expectable that they exhibit excellent compatibility with polymer electrolyte like Nafion in their interfaces. So the fabricated SPPEK mats will hold immense future applications as porous supporting substrates in PEM of fuel cells. And the experiments of filling SPPEK mats with polymer electrolyte like Nafion are underway.

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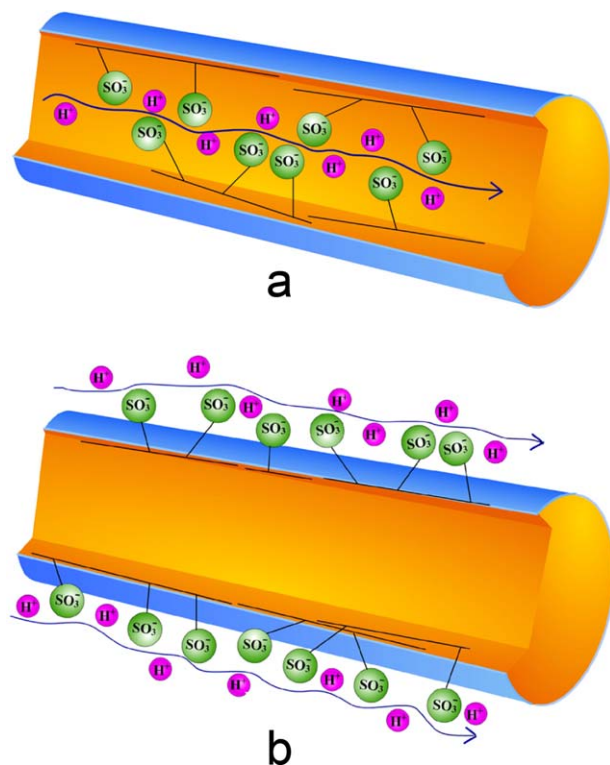14. Nguyen, T.; Wang, X. *J. Power Sources* **2010**, *195*, 1024.

Figure 4. Two possible mechanisms of long-range proton pathways formed during electrospinning of SPPEK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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