Ion Transport in Organic Electrolyte Solution through the Pore Channels of Anodic Nanoporous Alumina Membranes

Tomokazu Fukutsuka^{a,*}, Kohei Koyamada^a, Shohei Maruyama^a, Kohei Miyazaki^a, and

Takeshi Abe^{a, 1}

^a *Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510,*

Japan

* Corresponding author:

Tel +81-75-383-2483

Fax +81-75-383-2488

E-mail: fuku@elech.kuic.kyoto-u.ac.jp (Tomokazu Fukutsuka)

¹ ISE member

Abstract

For the development of high energy density lithium-ion batteries with the high rate performance, the enhancement of the ion transport in the electrolyte solutions impregnated in the porous electrodes is a key. To study the ion transport in porous electrodes, anodic nanoporous alumina (APA) self-standing membranes with macro- or meso-pores were used as model porous materials. These membranes had nearly spherical pore channels of discrete 20-68 nm in diameters. By using the geometric shape of the pores, we attempted to evaluate the specific ion conductivities of the organic electrolyte solution dissolving lithium salt simply. AC impedance spectroscopy measurement of a four-electrode cell with membranes showed one depressed semi-circle in the Nyquist plots and this semi-circle can be assigned as the ion transport resistance in the pores. The specific ion conductivities evaluated from the ion transport resistances and the geometric parameters showed very small values, even in the macro-pores, as compared with that of the bulk electrolyte solution.

Keywords

Ion transport, anodic nanoporous alumina membrane, meso-macro pores, lithium-ion battery electrolyte solution

1. Introduction

Large-size rechargeable batteries can be utilized for the efficient storage of renewable energy, thus helping in the creation of a sustainable society. As high-performance rechargeable batteries, large-size lithium-ion batteries (LIBs) have been developed for use in battery electric vehicles (BEVs) and stationary electronic power supplies. For BEVs, a long cruising distance and short charging time are imperative. The former is determined by the energy density (the product of battery voltage and battery capacity), and the latter is determined by the power density (the product of voltage and current). Present LIBs for use in BEVs possess large power densities at the expense of energy density. On the other hand, recent LIBs that are widely used for portable devices have large energy and small power densities. The important difference between these two types of LIBs is the charging time. In the case of LIBs for use in BEVs, shorter charging times are necessary, because the time spent pumping fuel into a traditional vehicle is just several minutes. To shorten the charging time, a reduction of the internal resistances in such LIBs is required.

The main components of LIBs are positive and negative electrodes, a separator, and an electrolyte solution. In LIBs, positive and negative electrodes are composed of active material, conductive additive, and binder coated onto the current collector and

these electrodes are porous electrodes. The internal resistances in LIBs are the results of various processes: (1) electron transfer between a current collector and an active material, (2) electron transport in a porous electrode, (3) ion (lithium ion and counter anion) transport in electrolyte solution impregnated in a porous electrode, (4) lithium-ion transfer at the interface between the active material and the electrolyte, (5) lithium-ion diffusion in the active material, and (6) ion (lithium ion and counter anion) transport in bulk electrolyte through the separator. The electron transfer of process (1) is usually very fast or at least is designed to be fast by the use of a carbon-coated current collector. Moreover the electron transport of process (2) is fast when the active materials show high electron conductivities. When the active materials possess poor electron conductive, such as LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, carbon coatings are employed as the active materials [1, 2]. By disregarding process (3) for a moment, we consider processes (4)–(6) in more detail. The fundamentals of process (4) have been studied by our group [3-14] and Xu's group [15-21]. Lithium-ion transfer, the so-called charge-transfer, resistances (R_{ct}) can be denoted by:

$$\frac{1}{R_{ct}} \propto A \exp\left(\frac{-E_a}{RT}\right) \quad \text{Eq. 1}$$

where A , E_a , R , and T are the pre-exponential factor, activation energy, gas constant, and absolute temperature, respectively. The R_{ct} is influenced by the E_a , the number of

reaction site, the lithium ion activity, electrode potential, and so on. Our and Xu's groups have shown that the de-solvation process is responsible for E_a [3, 4, 6, 9, 15]. In addition, we have previously shown that the Lewis basicity of the solvent has an important effect on E_a . This means that to decrease R_{ct} by a decrease in E_a a drastically-changing of the electrolyte solution is required, which is somewhat unrealistic for the present LIBs. The increase of A (related with the number of reaction site) by, for example, the use of fine particles, is an effective way to decrease R_{ct} . Lithium-ion diffusion (process (5)) resistances in the active materials cannot be ignored. However, graphite and LiCoO_2 (for example), which are typical negative and positive active materials, have been reported to show a very high rate capability when a single particle was used [22, 23]. In particular, high rates exceeding 1,000C were attained using single particles of graphite [22]. Some promising active material candidates, such as LiMnPO_4 , were reported to show quite low diffusion coefficients [24]; however, nano-sized particles can decrease the effective actual diffusion resistance. So far, the active materials used in commercial LIBs possess high diffusivities [22, 23, 25-31]. Ion transport resistances in the separator (process (6)) are also important, and these resistances can be controlled by the thickness and porosity of the separator. Therefore, processes (4)–(6) can be devised to overcome the issues outlined above. In relation to

the remaining process (3), ion transport resistances in electrolyte solution impregnated in porous electrodes are quite important in decreasing the internal resistances of LIBs (as described below); however, these have not been fundamentally investigated.

Ion transport in the porous electrode occurs in the impregnated electrolyte solution and proceeds through various pores in the porous electrodes. The morphology of pores is directly influenced by the structure of the electrodes [32]. The enhancement of energy density can be achieved by increasing the tap and loading densities of active materials in the porous electrodes. This means that thick and highly dense (low porosity) porous electrodes are essential for high energy density LIBs. In the porous electrode, the geometrical ion transport length in a thick porous electrode is longer than that in a thin porous electrode, and the longer ion transport lengths increase the ion transport resistance. In a high density porous electrode, the number of paths for ion transport becomes small and the pore sizes in the porous electrode are potentially decreased. In this case, ion transport resistance through the porous electrode must be increased, and the rate performance will be diminished. Striebel et al. reported the correlation between rate performance and the electrode density of a graphite negative electrode. They found that rate performance was diminished for high density electrodes [33].

The above considerations indicate that high energy density LIBs exhibit large ion transport resistances in porous electrodes, leading to a large internal resistance and low rate performance. In spite of this, it is necessary to achieve both a high energy density and a high power density for LIBs used in BEVs. Therefore, in order to overcome this problem, ion transport in electrolyte solutions impregnated in the porous electrode must be characterized. In other words, we must determine the specific ion conductivity of electrolyte solutions impregnated in porous electrodes consisting of macro-, meso-, and micro-pores to decrease the ion transport resistances in porous electrodes. The number and sizes of these pores are not evaluated individually in the porous electrodes; the pore parameters obtained from porous electrodes are based on averaged information and the connections between the pores are fairly complex. Therefore, we cannot define the cross-sectional area of pores and the length of ion transport paths and the specific ion conductivity of the electrolyte solutions impregnated in the porous electrode cannot be calculated. In spite of this situation, the ion transport in electrolyte solutions impregnated in the porous electrode is thought to be important and has been discussed in relation to the averaged structural parameters such as tortuosity and porosity and the ion conductivities were calculated based on these parameters. However, these reported ion conductivities are not the “specific ion

conductivities” but rather than “effective specific ion conductivities” [34]. Recently, Ogihara et al. [35] reported the effective specific ion conductivities of electrolyte solutions impregnated in porous electrodes by combining theory based on the transmission line model for cylindrical pores and an electrochemical impedance spectroscopy analysis. The effective specific ion conductivity was reported to be smaller than the specific ion conductivity of the bulk electrolyte solution. As is shown by the literature [34, 35], the effective specific ion conductivities of electrolyte solutions impregnated in porous electrodes are dependent on the structure of the porous electrodes. However, to date, there is no report on the specific ion conductivities of LIB electrolyte solutions impregnated in porous electrodes. The specific ion conductivities of LIB electrolyte solutions impregnated in porous electrodes might be influenced by the pore size, the chemical composition of pore, the concentration change in the pore, the electric field in the pore, and so on. As a first step to clarify the quantification of such specific ion conductivities, we focused on the pore size effects. Initially, we aim to evaluate the correlation between pore size and ion transport by using porous materials. To our knowledge, there is no report on the specific ion conductivities of LIB electrolyte solutions in the pore; hence, the results in this paper will offer a new insight for LIBs development.

In this paper, anodic nanoporous alumina (APA) self-standing membranes with one-dimensional through-holes were used as the model porous materials for the porous electrodes. In this case, the Bruggeman exponent [36] is unity and the simplest porous structure for quantitative analysis is evident. By using structural ordered APA self-standing membranes, the specific ion conductivities of electrolyte solutions thorough the pore channels in APA membranes with macro- and meso-pores were evaluated.

2. Experimental

2.1. Fabrication of APA self-standing membranes

APA sheets were synthesized using the two-step anodization process reported by Masuda and Fukuda [37]. A homemade two-electrode cell with Al sheet as a working electrode and Pt mesh as a counter electrode was used. The Al sheets (99.999%) of 0.5 mm thickness were cleaned by sonication in ethanol for 3 min. Electrochemical polishing was carried out in a mixture of perchloric acid and ethanol (1:4 by volume) below 5 °C under a constant cell voltage of 20 V for 3 min. The two-step anodization process was performed in 0.3 mol dm⁻³ oxalic acid aqueous solution under a constant cell voltage of 40 V. The electrolyte temperature was maintained below 5 °C during

anodization. The first anodization step was performed for 24 h. The initially grown alumina layer was dissolved in a phosphoric acid (6 wt%) and chromic acid (1.8 wt%) solution at 80 °C. The Al substrate, which had an ordered structure, was exposed to the second anodization step for 24 h. After the anodization process, the self-standing membrane was prepared according to the previous report of Xu et al. [38]. The alumina side of the obtained APA membrane was coated with nail polish as a protective layer. The APA membrane was first etched in a solution consisting of HCl (38%, 100 mL), H₂O (100 mL), and 3.4 g of CuCl₂·2H₂O for 3 h and then subsequently etched in 5 wt% phosphoric acid for 70 or 90 min. Finally, the protective layer was peeled off in acetone for 2 h. In order to remove absorbed water, the APA self-standing membrane was annealed in air at 500 °C for 3h. Hereafter, the APA self-standing membranes with phosphoric acid etching for 70 min and 90 min are denoted as APA-70 and APA-90, respectively.

2.2. Control of the pore sizes of APA self-standing membranes

Because of the high aspect ratios of APA self-standing membranes, the reduction of pore sizes does not proceed by ordinal liquid or vapor methods. Therefore, atomic layer deposition (ALD) was used [39]. The inside wall of APA-70 was coated with alumina using a custom-made ALD reactor (SUGA, Japan). The sources were

trimethyl aluminum (TMA) and ultrapure water. After evacuation of the reaction chamber, the APA-70s were heated, and the temperature was maintained at 300 °C. Water was introduced for 15 ms and evacuated for 5 s before TMA was introduced for 15 ms and evacuated for 5 s. During this process, TMA reacted with the absorbed water on the inside wall and was transformed to alumina by hydrolysis. By changing the number of times the above process was performed, the thickness of alumina layer was controlled; the cycle numbers were 100, 150, and 200. Hereafter, APA-70 subjected to the ALD process is denoted as APA-70-cycle number. Morphologies of the APA self-standing membranes were observed by scanning electron microscope with a field emission gun (FE-SEM; Carl Zeiss-SII, NVision 40); the pore sizes and thicknesses of the APA self-standing membranes were obtained.

2.3 Evaluation of specific ion conductivities

Ion transport resistances of the LIB electrolyte inside the APA self-standing membranes were measured by AC impedance spectroscopy by using a four-electrode cell. Figure 1 shows the four-electrode cell used in this study. The counter- and reference-electrodes were Li foil, and the electrolyte solution was 1 mol dm⁻³ LiClO₄/ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1 by volume). An APA self-standing membrane was sandwiched between the two vessels and was not subjected

to any electrical contact. Therefore, the membrane served only as an ion transport path, like a separator in a LIB. The contact area of the membrane and electrolyte solution was maintained at 0.50 cm^2 . The AC impedance spectroscopy measurement was conducted over a frequency region of 100 kHz–10 mHz with applied AC voltage amplitudes of 30–100 mV in an argon atmosphere. In this method, the resistance (R in Fig. 1), the sum of the resistance of the bulk electrolyte solution between R.E.1 and the APA self-standing membrane, the resistance of the electrolyte solution in the APA self-standing membrane, and the resistance of the bulk electrolyte solution between R.E.2 and the APA self-standing membrane, is obtained. In addition, the ion transport through a graphite composite porous membrane was investigated for comparison. A slurry of spherical natural graphite and polyvinylidene difluoride (PVdF) (9:1 weight ratio) was coated on perforated Cu foil with 70- μm pores. After drying, the composite porous membrane was roll pressed. The thickness and density of the membrane were 79 μm and 1.52 g cm^{-3} , respectively. The obtained graphite composite porous membrane was used as a self-standing membrane without peel off from the Cu foil. In the case of the graphite composite porous membrane, the applied AC voltage amplitude was set at 30 mV. Although the graphite composite porous membrane is electron conductive, there is no direct contact between the graphite composite porous membrane and the electrodes.

Hence, the graphite composite porous membrane functioned like the APA self-standing membrane.

3. Results

3.1. Morphology of APA self-standing membranes

Figure 2 shows a typical FE-SEM image of APA-70-0. In Fig. 2(a) and (b), ordered honeycomb structures were clearly observed on the top (anodized) side and the bottom (etched) side. In addition, the oblique section image in Fig. 2(c) shows that the pores penetrated from the top side to the bottom side. The pore size and thickness were 60 nm and 110 μm , respectively. Therefore, it can be concluded that ordered one-dimensional through-holes were successfully obtained. Figure 3 shows FE-SEM images of APA-70-150 and APA-90. In the Fig. 3(a), the pore size was reduced from 60 to 27 nm. The pore size was clearly controlled by the ALD process. Figure 3(b) shows an FE-SEM image of APA-90. The pore size was enlarged from 60 to 68 nm by etching. However, a longer etching time of over 90 min broke the wall causing neighboring pores to become connected. To obtain a larger pore-size APA self-standing membrane, the anodization conditions needed to be changed. However, different anodization conditions produce a different number of pores; therefore, the maximum pore size in

this study was limited to 68 nm. Table 1 shows the structural parameters obtained from FE-SEM images of the APA self-standing membranes (pore diameter D , wall to wall distance W , and pore length L). Pore sizes were controlled and ranged from 20 to 68 nm in this study.

3.2. AC impedance spectroscopy measurement of APA self-standing membranes

Initially the AC impedance response of the four-electrode cell was investigated. Figure 4 shows the Nyquist plots for the four-electrode cell without the APA self-standing membrane (blank cell) ([a]: filled circle) and with a commercialized separator ([b]: open circle). The shape of the two Nyquist plots was similar without the intercept of Z' axis and the points were scattered around the intercept of Z' axis, which corresponds to ohmic resistance. The ohmic resistance for [a] was larger than that for [b], but this was within the error and is due to differences in cell fabrication. This implies that the commercial separator did not change the shape of the Nyquist plot in this measurement. Next, the AC impedance response of the four-electrode cell with an APA self-standing membrane was obtained. Figure 5 shows the Nyquist plot for APA-70-0. In contrast to Fig 4, one depressed semi-circle was observed at all AC voltages. This indicates that this depressed semi-circle was caused by the ohmic processes related to ion transport through the pores in APA-70-0. Interestingly, the

appearance of semi-circle indicated that a capacitive element existed and it is associated with the ion transport process in the pores, despite that the APA self-standing membrane is an insulator. Although we have no clear understanding of this capacitive element at the present time, further study is underway. Since a portion of the semi-circle appeared in the higher frequency region in Fig. 4, it should be considered that the higher frequency region of the semi-circle is not related to ion transport through the APA self-standing membrane. Then, the lower frequency region of the semi-circle was assigned as ion transport through the pores and it was simply fitted using one semi-circle, as shown in Fig. 5 (dotted line). The ion transport resistance through the pores was calculated to be 140 Ω . In the cases of the commercial APA self-standing membrane and the APA self-standing membrane with disordered pore sizes, Nyquist plots without semi-circles were sometimes observed. This is probably because ions would move more readily through the simpler paths in the APA self-standing membrane. Therefore, the use of an APA self-standing membrane with homogenous pore sizes is likely to be important for this measurement. Other APA self-standing membranes (except for APA-70-200) showed the similar Nyquist plots, and the ion transport resistance through the pores R and capacitance within the pores C were obtained. Although APA-70-200 showed a pore diameter of 20 nm, a semi-circle assignable to ion

transport was not obtained. In addition, a similar Nyquist plot was observed for the graphite composite porous membrane as shown in Fig. 6. Since this semi-circle was depended on the thickness and densities of membranes, we can assign this semi-circle as ion transport in the membrane. Therefore, it can be thought that the semi-circles obtained in APA self-standing membranes would relate with the ion transport in the graphite composite porous membrane. The difference is the characteristic frequency. The graphite composite porous membrane gave 6 Hz and this is smaller than that of APA-70-0 in spite of similar ion transport resistances. This difference would be the difference of the capacitance derived from the inner area, although we cannot define the inner area of the graphite composite porous membrane.

4. Discussion

APA self-standing membranes have an ordered structure; hence, various geometrical parameters can be calculated. By using pore diameter D , wall to wall distance W , and pore length L (Table 1), the specific ion conductivities and specific capacitances were calculated as follows. Figure 7 shows a schematic illustration of the surface of an APA self-standing membrane. The area of a honeycomb $s_{\text{honeycomb}}$, the area of a pore s_{pore} , the number of honeycombs $N_{\text{honeycomb}}$, the total pore area S_{pore} can be

obtained using the equations in Fig. 7. By using these values, the porosity P , specific ion conductivity κ , and specific capacitance; C_s are calculated using Eqs. 2, 3, and 4, respectively.

$$P = \frac{S_{\text{pore}}}{S_{\text{total}}} \quad \text{Eq. 2}$$

$$\kappa = \frac{L}{RS_{\text{pore}}} \quad \text{Eq. 3}$$

$$C_s = \frac{C}{\pi LDN_{\text{honeycomb}}} \quad \text{Eq. 4}$$

The calculated values are shown in Table 2. The specific ion conductivities of electrolyte solutions in the macro- and meso-pores were not dependent on pore size and showed similar values. The same tendency was observed for the specific capacitances; therefore, capacitive element was thought to exist at the inner of pores. Surprisingly, the specific ion conductivities of the electrolyte solutions in the pores were an order of magnitude smaller than that of the bulk electrolyte solution (7.6 mS cm^{-1}). For the first time, therefore, we have shown drastic decrease in the specific ion conductivities of LIB electrolyte solutions inside 27 to 68 nm pores. It has been previously reported that the specific ion conductivities of KCl or NaCl aqueous solutions inside the pores of alumina membranes or oyster shells are increased, as compared with bulk electrolyte solutions, when the concentration of the electrolyte solution is low [40, 41]. In the case of aqueous solutions, the interaction between the charged pore wall and the ion is reported to

facilitate ion transport. Based on such reports [40, 41], a decrease in the specific ion conductivity of LIB electrolyte solution inside 27 to 68 nm pores seems to be a unique phenomenon. Indeed, the lithium-ion transportation numbers evaluated using the same cell were 0.34 and 0.33. These values are almost the same as the bulk electrolyte solution. Hence, the interaction previously reported for an aqueous solution was not evident in this study. To explain the decrease in specific ion conductivities, the decrease in the carrier number (the number of mobile ions) in the electrolyte solutions in the pores was first considered since the physicochemical properties of the electrolyte solution, such as the solvation structure of the ion, the dissociation degree of the lithium salt, and so on, are changed in the limited space. However, we have no experimental evidence to support this hypothesis at the present time. The effect of the electric double layers on the pore walls can be also considered, but the pore radii are too large for the Debye length. So far, the specific capacitances and interactions between the pore walls and the LIB electrolyte solutions have not been clarified. The interaction between the electrolyte solution and pore walls has been studied experimentally and theoretically; the detailed analysis will be reported in the future. Although the reason of the decrease of specific ion conductivities of the LIB electrolyte solution in macro- and meso-pores is not clarified at the present stage, this underlying mechanism influence to the ion

conduction in the porous electrode and must be considered in the development of large-size LIBs.

5. Conclusion

The specific ion conductivities of LIB electrolyte solution in macro- and meso-pores were evaluated using ordered APA self-standing membranes. The APA self-standing membranes synthesized by using two-step anodization showed ordered honeycomb structures with 27 to 68 nm pore diameter. The Nyquist plots obtained using a four-electrode cell with APA self-standing membranes showed one depressed semi-circle. The lower frequency region of the depressed semi-circle was assigned to ion transport resistance through the pores of the APA self-standing membranes. The calculated specific ion conductivities of the LIB electrolyte solution in macro- and meso-pores were not dependent on pore size and it was revealed for the first time that the specific ion conductivities of LIB electrolyte solution inside the pores were an order of magnitude smaller than that of the bulk electrolyte solution. Although, the ion conduction in this study might not be the same as that in the porous electrodes of LIBs in the operating mode, since the chemical composition, the concentration variation, the electric field, and so on should be taken into considered to fully understand the specific

ion conductivities of LIB electrolyte solutions impregnated in the porous electrodes.

However, we believe that our finding is quite important for the first step to investigate the ion conduction in the porous electrodes.

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Figure captions

Table 1

Structural parameters of APA self-standing membranes obtained from FE-SEM images

Table 2

Calculated porosity, specific ion conductivity, and specific capacitance from Table 1 and Nyquist plots

Figure 1

Schematic illustration of a four-electrode cell for AC impedance spectroscopy measurement.

Figure 2

FE-SEM images of APA-70-0: (a) top side, (b) bottom side, and (c) oblique section images.

Figure 3

FE-SEM images of the top side of (a) APA-70-150 and (b) APA-90.

Figure 4

Nyquist plots for a four-electrode cell without membrane [a] and with commercial separator [b].

Figure 5

Nyquist plots for a four-electrode cell with APA-70-0. The dotted line semi-circle is the fitted semi-circle.

Figure 6

Nyquist plot for four-electrode cell with a graphite composite electrode.

Figure 7

Model of an APA-self-standing membrane for calculating the structural parameters.

Table 1 T. Fukutsuka et al.

Structural parameters of APA self-standing membranes obtained from FE-SEM images

	Pore diameter D (nm)	Pore distance W (nm)	Pore length L (μm)
APA-90	68	27	130
APA-70-0	60	35	110
APA-70-100	35	60	120
APA-70-150	27	68	130
APA-70-200	20	75	125

Table 2 T. Fukutsuka et al.

Calculated porosity, specific ion conductivity, and specific capacitance from Table 1 and Nyquist plots

	Porosity P (%)	Specific ion conductivity κ (mS cm ⁻¹)	Specific capacitance C_s (nF cm ⁻²)
APA-90	46	0.48	3.7
APA-70-0	36	0.55	11
APA-70-100	12	0.46	7.4
APA-70-150	7.3	0.44	9.4
APA-70-200	4.0	-	-

APA self-standing membrane

Figure 1 T. Fukutsuka et al.

Schematic illustration of a four-electrode cell for AC impedance spectroscopy measurement.

Figure 2 T. Fukutsuka et al.

FE-SEM images of APA-70-0: (a) top side, (b) bottom side, and (c) oblique section images.

Figure 3 T. Fukutsuka et al.

FE-SEM images of the top side of (a) APA-70-150 and (b) APA-90.

Figure 4 T. Fukutsuka et al.

Nyquist plots for a four-electrode cell without membrane [a] and with commercial separator [b].

Figure 5 T. Fukutsuka et al.

Nyquist plots for a four-electrode cell with APA-70-0.
The dotted line semi-circle is the fitted semi-circle.

Figure 6 T. Fukutsuka et al.

Nyquist plot for four-electrode cell with a graphite composite electrode.

APA self-standing membrane

Defined reaction area : S_{total}

$$\left\{ \begin{array}{l} s_{\text{honeycomb}} = \frac{\sqrt{3}}{2} (D + W)^2 \quad s_{\text{pore}} = \frac{1}{4} \pi D^2 \\ N_{\text{honeycomb}} = \frac{S_{\text{total}}}{s_{\text{honeycomb}}} \quad S_{\text{pore}} = N_{\text{honeycomb}} \times s_{\text{pore}} \end{array} \right.$$

Figure 7 T. Fukutsuka et al.

Model of an APA-self-standing membrane for calculating the structural parameters.