

Nanofiller-Based Novel Hybrid Composite Membranes for High-Capacity Lithium-Sulfur Batteries

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Herein, Al₂O₃ nanofiller-reinforced lithiated Nafion:Aquivion hybrid composite ion-exchange membranes have been produced by mixing lithiated Nafion and Aquivion ionomers. After the electrochemical tests, the Li-Naf:Li-Aqu/1:2 compound, which offers the best electrochemical performance, was selected. Lithiated hybrid composite membranes were obtained by reinforcing Al₂O₃ nanofillers at different rates to this composition. The ion exchange capacity, polysulfide transition and solvent uptake of the obtained membranes were investigated and the structural characterizations were applied by tensile test, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and membrane morphology was exam-

ined with Field Emission Scanning Electron Microscopy (FESEM). For performing the electrochemical tests, CR2032 half cells were designed. Electrochemical characterizations of the produced membranes were carried out by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and galvanostatic charge-discharge tests. The best electrochemical performance was achieved with 868 mAhg⁻¹ discharge capacity and 63.8% capacity retention when Li-Naf:Li-Aqu/1:2 composition was reinforced with 1% Al₂O₃ nanofiller. As a result, lithiated hybrid composite ion exchange membranes could prevent the shuttle effect of polysulfides while enabling the passing of Li ions for high-performance Li-S batteries.

Introduction

Li-S batteries are accepted as new generation energy storage devices with superior theoretical capacity and energy density and are also suitable for use in electric and hybrid electric vehicles.^[1,2] In addition, sulfur is the seventeenth most prosperous element in the earth's crust and does not require much processing to purify it, making it available at a low cost. Another important property of elemental sulfur is its very low toxicity, making it notable among all materials used for batteries and other electronic devices.^[3] Li-S batteries operate by electrochemical reduction of sulfur to polysulfides, forming insoluble Li₂S₂ or Li₂S precipitates.^[4]

However, besides the advantages of this energy storage system, it also has several issues. The difficulties to overcome are the conductivity problem of sulfur and its solid reduction products Li₂S₂ and Li₂S and the high solubility of the

intermediate products that occurred during the lithiation of sulfur in liquid-electrolyte systems. Intermediates with high solubility in the electrolyte cause the "shuttle effect". This effect is defined as the migration of polysulfides to the negative electrodes, where the polysulfides are partially reduced. The short polysulfides then migrate back to the positive electrode, where they are reoxidized, causing low coulombic efficiency and self-discharge of the cell.^[5] Therefore, mobile polysulfides circulate between the electrodes, causing the charging time of the battery to reach infinity. To this end, Nafion and Aquivion, proton exchange membranes, could be used in Li-S batteries. Both ionomers consist of perfluoroether side chains with sulfonic acid groups attached to the perfluoroethylene backbone. However, vary differ in terms of side-chain length and equivalent weight. Nafion belongs to the long side chain (LSC) ionomer group, while Aquivion is known as a short side chain (SSC) ionomer. Equivalent weight refers to the weight of the membrane (1100 EW: 1100 g/mol -SO₃H) per 1 mole of -SO₃H molecule at the end of the side chain. In addition to the difference in side chain lengths, the equivalent weight also affects conductivity and performance.^[6,7] Ion exchange membranes attract attention, especially in Li-S batteries, because they can be used to limit polysulfide diffusion by preventing the shuttle movement of polysulfide between positive and negative electrodes.^[8]

It is known that Al₂O₃ has the ability to trap polysulfides.^[9] Thanks to its porous structure and absorption capacity, Al₂O₃ can be used as a sorbent to absorb polysulfides to increase the electrochemical performance of the cells during the charge-discharge process.^[10-12] In addition, its porosity can provide plenty of channels for the passage of lithium ions. Therefore, when cation-selective Nafion, Aquivion membrane, and porous Al₂O₃ are used together, it is expected to advance the electrochemical feature of the cell. Also, by varying the Al₂O₃ content,

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the electrochemical performance of the cell can improve.^[13] In this study, trapping polysulfides in Li–S battery by using lithiated Nafion (Li-Naf) and lithiated Aquivion (Li-Aqu) membranes as electrolyte and separator was investigated. By reinforcing Al_2O_3 nanofillers to the Li-Naf:Li-Aqu/1:2 membrane, hybrid composite membranes were obtained, and structural and electrochemical characterizations were carried out.

Experimental Section

The fabrication of hybrid composite membranes

The first step in preparing ion-exchange hybrid composite membrane electrolytes is the lithiation of Nafion and Aquivion ionomer solutions. The second step is to obtain Li-Naf and Li-Aqu ionomer powders from lithiated solutions. The third stage is the production of hybrid composite membranes by reinforcing Al_2O_3 nanofiller at different ratios to the Li-Naf:Li-Aqu/1:2 composite selected due to electrochemical tests in our previous study.^[14]

Li-Naf and Li-Aqu ionomer powders were prepared as mentioned in our previous work.^[14] Al_2O_3 as a nanofiller was purchased commercially (< 50 nm, Aldrich) and added to the Li-Naf:Li-Aqu/1:2 composite at different weight ratios. For this purpose, Li-Naf and Li-Aqu powder ionomers were weighed at a ratio of 1:2 by weight, and Al_2O_3 was added as 0.5%, 1%, 2%, and 3% by weight of the total ionomer amount. After adding a calculated amount of DMF to it, it was first heated at 50 °C, mixed, and provided dissolving in DMF. To ensure homogeneous distribution of Al_2O_3 nanofiller into the ionomer mixture, it was kept in an ultrasonic bath for 2 hours. Then, it was mixed in the heater to reach the appropriate consistency and poured into Petri dishes. After the film was obtained by evaporating the solvent at 80 °C, annealing was carried out to develop the membrane's flexibility and durability by keeping it in an oven at 150 °C for 12 hours. Finally, the films produced were adequately taken from the glass surface. The

addition of Al_2O_3 to the membrane was compared with the Li-Naf:Li-Aqu/1:2 (0% Al_2O_3). The preparation method of the produced Al_2O_3 nanofiller reinforced hybrid composite membranes is given schematically in Figure 1.

The codes given for the produced membranes are shown in Table 1. For example, the lithiated hybrid composite membrane (in Li-form) with 0.5% Al_2O_3 reinforcement to Li-Naf:Li-Aqu/1:2 is expressed as Li-0.5, while the Li-Naf:Li-Aqu/1:2 without Al_2O_3 nanofiller is indicated as Li-0.

For characterizing lithiated hybrid composite membranes (Li-form) by comparing them with protonated hybrid composite membranes (H-form), 0.5%, 1%, 2%, and 3% Al_2O_3 nanofiller reinforced H-form Naf:Aqu/1:2 hybrid composite membranes were also produced without lithiation process. In addition, the Naf:Aqu/1:2 membrane (0% Al_2O_3) without Al_2O_3 nanofiller was produced to be compared with other membranes. The codes given for the produced H-form membranes are shown in Table 2.

Membrane characterizations

The ion exchange capacity (IEC) expresses the quantity of $-\text{SO}_3\text{H}$ (mmol) per gram of the membrane. The IEC of protonated membranes was defined by the traditional titration technique.^[15] The change in IEC of H-form membranes with the addition of Al_2O_3 to the Naf:Aqu/1:2 membrane was investigated. For this purpose, 0% Naf:Aqu/1:2 membrane and 0.5%, 1%, 2% and 3% Al_2O_3 nanofiller reinforced hybrid composite membranes were compared. Each of these membranes was dried at 80 °C for 12 hours, and their weights were measured, then dipped in NaCl solution (2 M) and held there for 24 hours. During the waiting phase, the H^+ ions present in Nafion and Aquivion membranes were replaced with the Na^+ ions. These H^+ ions were titrated with NaOH solution (0.01 M) adjusted against potassium hydrogen phthalate to the endpoint with phenolphthalein. Taking into account the NaOH consumption, the IEC of the membranes was calculated in mmol/g via Equation 1. Here, V_{NaOH} denotes the NaOH consumption (mL) in the titration, the C_{NaOH} the NaOH concentration (M) used, and the m_{dry} expresses

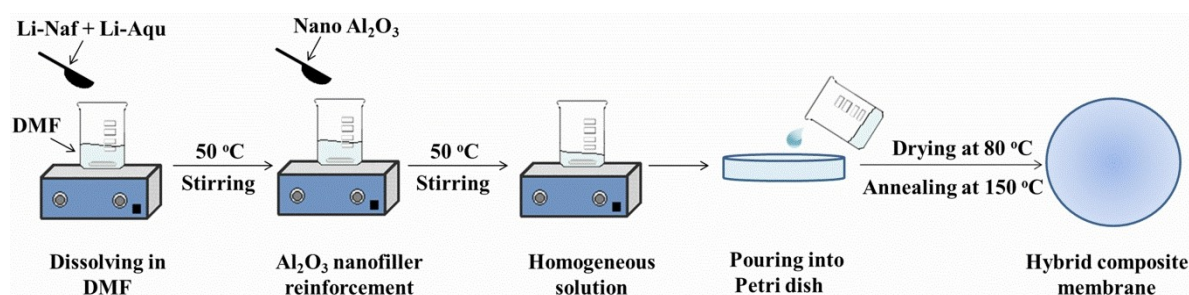


Figure 1. Production stages of the membranes.

Table 1. Codes for samples with Al_2O_3 added to the Li-Naf:Li-Aqu/1:2.

Al_2O_3 nanofiller (%)	Sample Name
0	Li-0
0.5	Li-0.5
1	Li-1
2	Li-2
3	Li-3

Table 2. Codes for samples with Al_2O_3 added to the Naf:Aqu/1:2 membrane.

Al_2O_3 nanofiller (%)	Sample Name
0	H-0
0.5	H-0.5
1	H-1
2	H-2
3	H-3

the weight in grams of the membrane weighed initially in the dry state.

$$\text{Membrane ion exchange capacity} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{m_{\text{dry}}} \quad (1)$$

When the ion exchange membranes, which are produced to be used as separators and electrolytes in lithium batteries, are kept in a mixture of organic solvents which has a high value of a dielectric constant, the swelling process is applied, and the membrane absorbs these solvents. Thus, improved battery performance is achieved as a result of membranes reaching higher conductivity values.^[16] For this reason, before being used in Li–S batteries, the membranes were swelled by keeping them in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) solvent mixture. In addition to the type of solvent chosen for the swelling of the membrane, the amount of solvent taken into the membrane is also crucial in increasing the conductivity. The swelling behavior of H-form hybrid composite membranes with the addition of Al₂O₃ to the Naf:Aqu/1:2 membrane was investigated. H-0, H-0.5, H-1, H-2 and H-3 hybrid composite membranes were cut into circles with a diameter of 19 mm and dried in a vacuum oven at 105 °C for 12 hours, and their dry weights were weighed. After the membranes were kept in 1/1 (w/w) DME/DOL solvent mixture at room temperature for 24 hours, they were taken out from the solvent mixture. The excess solvent remaining on the membrane surface was removed using filter paper. Then, the weights of the membranes, swollen with solvent, were quickly measured. The solvent uptake of the membrane was calculated taking into account the Equation 2. Here, m_1 represents the dry weight of the membrane, while m_2 represents its weight in the swollen state with solvent.

$$\text{Solvent Uptake (\%)} = \frac{m_2 - m_1}{m_1} \times 100 \quad (2)$$

As it is known, the sulfur cathode creates soluble polysulfides during the reduction reactions that occurred during discharge, causing a capacity loss in the Li–S cells. For this purpose, membranes that allow lithium-ion passage but prevent polysulfide passage have been developed to trap the formed polysulfides and obstruct their transition from the separator to the anode side. By using the system containing two cylindrical glass cells, the polysulfide diffusion through the produced ion exchange membranes was optically determined and compared with the traditional polypropylene (PP) separator. Polysulfide solution (Li₂S₈) was filled in one of these cells and the other with the basic electrolyte. PP separator, Li-Naf:Li-Aqu/1:2, and 1% Al₂O₃ nanofiller reinforced membrane were placed between these two cells, respectively. The ability of the PP separator and membranes between the two cells to hinder the passage of polysulfide solution to the other cell was investigated.

The tensile test was applied to determine the membranes' mechanical properties by using a uniaxial test system (Instron 3367). The thickness, length, and width of the samples were measured by using a Mitutoyo micrometer. A necessary clamping area was provided to compress both sides of each 10 mm×50 mm membrane, and the samples were prepared by cutting in the bone-shaped so that the test area was 5 mm×10 mm. All the samples were tested in a tensile device with a constant strain rate of 20 mm/min.

Rigaku D/MAX/2200/PC model X-ray diffractometer with CuK α radiation of $\lambda = 1.54050 \text{ \AA}$ and 2°/min scanning speed was used for XRD analysis. PerkinElmer Spectrum Two model FT-IR spectroscopy was used for optical measurements. The produced membranes'

morphologies were examined via FEI QUANTA 450 model field emission gun-scanning electron microscopy (FEG-SEM).

Electrochemical characterizations

Using the produced membranes, CR2032 button cells were designed in an Ar-filled glove box (MBraun-Labstar) to determine the electrochemical performances in Li–S batteries. S/rGO/CNT composite was used as cathode that we stated in our previous work^[17] and metallic lithium was utilized as anode. Produced lithiated membranes were used to perform both separator and electrolyte functions in the cell. Before assembling the cells, the membranes were held in DME:DOL solution for 24 h. To perform the electrochemical characterization, a battery tester (BST8-MA MTI) was used within the 3.0 V–1.5 V for 300 cycles with a rate of 0.1 C. Cyclic voltammetry (CV) measurement was applied at the scan rate of 0.1 mVs⁻¹ between the same voltage ranges.

The electrochemical stability of the lithiated hybrid composite membrane was specified by CV between –0.5 V and +5.0 V voltage limits at the scan rate of 0.1 mVs⁻¹. Lithium metal was used as the counter and reference electrode, and stainless steel (SS) was utilized as the working electrode. By clamping the membrane between two SS electrodes, electrochemical impedance spectroscopy (EIS) were applied to determine the ionic conductivity over a frequency range of 1000 kHz–0.1 Hz with an amplitude of 10 mV. Conductivities were calculated with Equation 3. Where l expresses the distance between two electrodes, A the cross-sectional area of the membrane, and R the resistance.^[18] OrigaFlex OGF500 model OrigaLys ElectroChem SAS was employed for both CV and EIS analyses.

$$\sigma = \frac{l}{R \times A} \quad (3)$$

Results and Discussion

Membrane characterizations

Ion exchange capacity, solvent uptake, and polysulfide transition

IEC of Al₂O₃ reinforced H-form hybrid composite membranes were specified by the conventional titration method. It is known that the IEC, which expresses the amount of –SO₃H in mmol per unit gram of the membrane, gives an idea about the ion exchange of the membrane. The IEC values of H-0, H-0.5, H-1, H-2, and H-3 membranes are given in Table 3. As can be seen from the table, a significant increase was observed in the IEC values with the increase in the amount of nano Al₂O₃ reinforced

Table 3. IEC values of Naf:Aqu/1:2 membranes reinforced with different ratios of Al₂O₃.

Membrane	IEC (mmol/g)
H-0	1.12
H-0.5	1.24
H-1	1.33
H-2	1.39
H-3	1.42

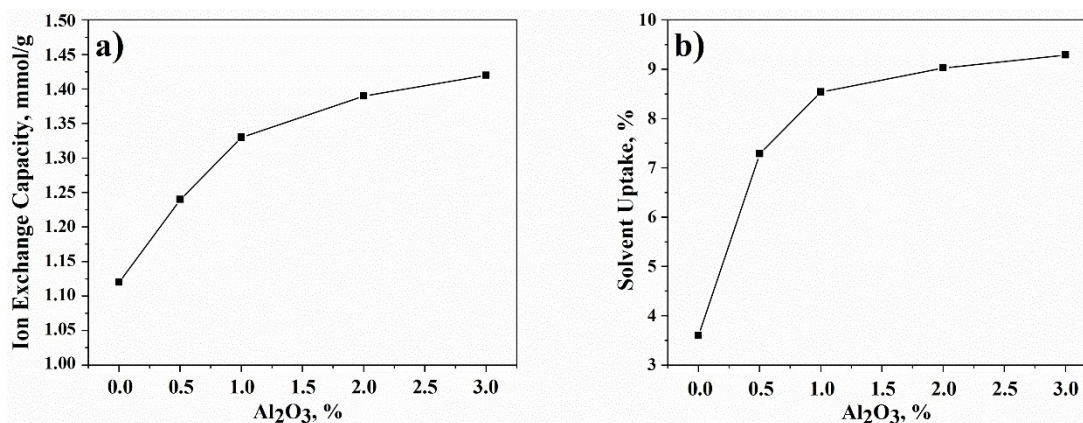


Figure 2. (a) IEC values of Naf:Aqu/1:2 membranes reinforced with Al₂O₃ at different rates; (b) Solvent uptake values of membranes.

to the membrane. Accordingly, IEC values are varies as 1.12 for H-0; 1.24 for H-0.5; 1.33 for H-1; 1.39 for H-2, and 1.42 for H-3.

Figure 2(a) also shows the increase in ion exchange capacity with Al₂O₃ reinforcement applied to the membranes. It is expected that the nano-structured Al₂O₃ (Figure S1, Figure S2) will contribute to the ion density in the membrane, thus increasing the IEC.^[19] Since Al₂O₃ nanofiller reinforcement to the H-form membrane will provide a new acidic zone,^[20] it is expected that the IEC will increase as a result of the increase in the H⁺ ion exchange capability of the membrane as the amount of reinforced Al₂O₃ increases. From this point of view, it is concluded that Al₂O₃ reinforcement to the Naf:Aqu/1:2 membrane is carried out successfully. On the other hand, while the increase in ion exchange capacity is higher in 0.5% and 1% Al₂O₃ reinforcement, the rise in ion exchange capacity is lower in membranes with 2% and 3% Al₂O₃. As the amount of Al₂O₃ reinforced to the membrane increased, it is observed that there was not much increase in the IEC values since the membrane is saturated in terms of nanofiller.

When ion-exchange membranes are used directly as separators and electrolytes in lithium batteries, conductivities of these membranes are insufficient for the applicability of the battery. However, when these membranes are swollen by keeping them in organic solvents with a high dielectric constant, the ionic conductivity of the membranes increases.^[21,22] For this reason, ion exchange membranes were swelled in a DME:DOL mixture before being used in Li-S cells. The swelling phenomenon causes the volume to expand as the solvent molecules penetrate the ionomer, weakening the interaction of ionomers with each other and increasing the distance between the molecules.^[23] The presence of solvent affects the ionomer microstructure, cluster, channel size and improves the properties of the membrane.^[20] For this reason, increasing the amount of solvent uptake into the membrane during the swelling will also contribute to the rise in the ionic conductivity of the membrane.^[21] In Table 4, solvent uptake (%) values are given after swelling of the Al₂O₃ nanofiller reinforcement hybrid composite membranes and the Naf:Aqu/1:2 membrane in a DME/DOL solvent mixture. In Figure 2(b), the solvent uptake values of these membranes are also given.

Table 4. Solvent uptake values of membranes reinforced with Al₂O₃ at different rates.

Membrane	Solvent Uptake (%)
H-0	3.60
H-0.5	7.29
H-1	8.54
H-2	9.03
H-3	9.29

When Table 4 is examined, it can be seen that the solvent uptake for the H-0 membrane is 3.6%, while it increases up to 9.29% as the amount of Al₂O₃ nanofiller reinforced to the membrane increases. From here, it is seen that the solvent retention capacity of the membrane increases as the amount of Al₂O₃ nanofiller increases. This situation is explained by the fact that Al₂O₃ can retain a significant amount of solvent molecules. However, as seen in Table 4, while the increase in solvent retention capacity is higher in H-0.5 and H-1 membranes, the increase is lower for H-2 and H-3 membranes. From this, it is understood that when the amount of Al₂O₃ reinforced to the membrane rises above a certain value, it does not cause a significant increase in the solvent retention capacity. Therefore there is no need to reinforce large amounts of Al₂O₃ to the membrane.

In Li-S batteries, it is known that soluble polysulfides are formed in the liquid electrolyte in the course of the discharging process. These dissolved polysulfide species pass through the traditionally used polypropylene (PP) separator and shuttle through the anode and the cathode, and this causes the performance of Li-S batteries to decrease.^[24,25] For this purpose, Al₂O₃ nanofiller reinforced Li-Naf:Li-Aqu/1:2 membranes have been developed to be used both as separators and as electrolytes, which prevent the transition of PS species occurred during the operation of the battery to the anode but allows the transition of lithium ions. In Figure 3, images of polysulfide diffusion measurements of traditionally used PP separator, Li-Naf:Li-Aqu/1:2 and 1% Al₂O₃ reinforced Li-Naf:Li-Aqu/1:2 membranes are given. Here, while the prepared Li₂S₈ polysulfide

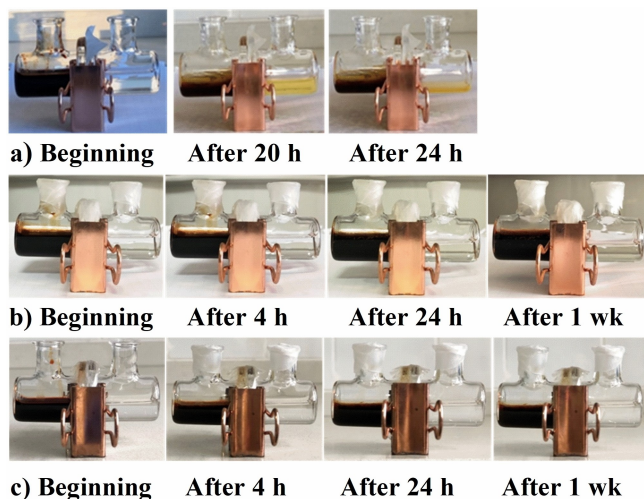


Figure 3. Polysulfide diffusion process through (a) PP separator; (b) Li-0 membrane; (c) Li-1 membrane.

solution is filled in the left side of the cell, the electrolyte is filled in the right side, and the ability of PP and membranes placed between the two cells to prevent the diffusion of polysulfide species over time was examined.

In Figure 3(a), it can be seen that the red-brown high-grade polysulfides (PS) on the left side of the cell diffuse through the other side along the concentration gradient due to the pore sizes that allow the dissolved PS species of the PP separator to pass from the cathode to the Li metal anode. Although only 20 hours have passed, it can be seen that PS species have passed through the separator. Thus, the electrolyte on the right turns yellow from colorless. After 24 hours, the electrolyte's color has wholly turned yellow. From this, it is clearly seen that the Polypropylene separator could not obstruct PS diffusion in Li-S batteries. On the contrary, when Li-0 and Li-1 membranes are placed between the two cells in Figure 3(b) and 3(c), it can be seen that the electrolyte remains colorless in the right side even after waiting for one week. As a result, the produced membranes make it possible to obtain high-capacity batteries by preventing polysulfide diffusion, which causes a significant decrease in the performance of Li-S batteries.

Structural characterizations

Tensile test was applied to have information about the rigidity of the produced hybrid composite membranes. The graph of the strain values against stress values in the membranes is given in Figure 4. From this graph, the point where the elastic and plastic deformation lines intersect is determined as the elastic deformation limit,^[26] and these values are given for each membrane in Table 5.

When Table 5 is examined, while the elastic deformation limit is 11.7 MPa for the composite membrane (H-0) without Al₂O₃ reinforcement, this value is 13.6, 13.8, 14.5, and 15.5 MPa for H-0.5, H-1, H-2, and H-3 membranes, respectively. As the amount of Al₂O₃ reinforced to the membrane increased, the

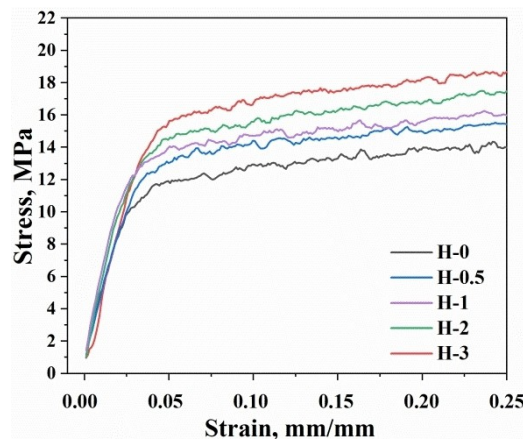


Figure 4. Stress-strain curves of membranes reinforced with different ratios of Al₂O₃.

Table 5. Elastic deformation limits of produced membranes.

Membrane	Elastic Deformation Limit (MPa)
H-0	11.7
H-0.5	13.6
H-1	13.8
H-2	14.5
H-3	15.5

amount of applied force against the unit elongation amount of the membrane increased due to the interaction between Al₂O₃ and the membrane. As a result of increasing the reinforcement of Al₂O₃ as a nanofiller to the membrane, it is seen that the durability of the membrane increases, and its mechanical properties improve. However, since the membrane structure is too rigid, it will reduce ionic interactions.^[27] If the membrane is used as an electrolyte, it is considered that large amounts of nanofiller reinforcement will make Li⁺ ion transition difficult. For this reason, it will be important to keep the amount of Al₂O₃ reinforced to the membrane at an optimum level. From this point of view, when Table 5 is investigated, it can be seen that the elastic deformation limit values of the H-0.5 and H-1 membranes are close to each other and lower, while these values are higher due to the high amount of reinforced Al₂O₃ in the H-2 and H-3 membranes. From this, it is concluded that 1% Al₂O₃ supplementation to the membrane will be an optimum value.

FTIR analysis was performed to examine the optical properties of NaF:Aqu/1:2 membranes with 0.5%, 1%, 2%, and 3% Al₂O₃ reinforced and without Al₂O₃ (H-0) and FTIR spectra of these membranes are given in Figure 5(a). The peaks seen at 1206, 1146, and 1053 cm⁻¹ for each membrane correspond to the asymmetric stretching of the CF₂ and SO₃⁻ groups, the asymmetric stretching of the CF₂ group, and the symmetrical stretching of the SO₃⁻ (belonging to the S-O bond) in the membranes, respectively. The peaks observed at 968 and 983 cm⁻¹ are attributed to the symmetrical stretching vibration

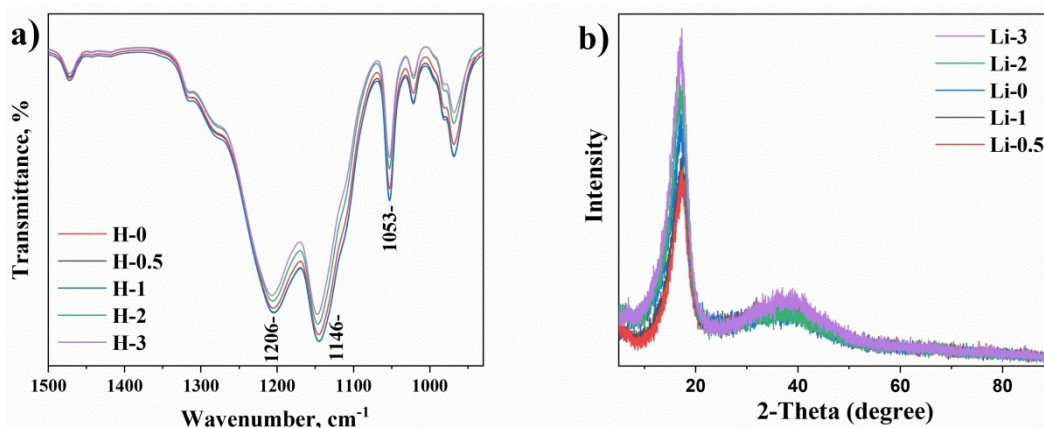


Figure 5. (a) FTIR spectra of produced H-form ion exchange membranes; (b) XRD diffractograms of produced membranes.

of the C–O–C bond.^[19,28–31] In addition, when the FTIR spectrum is examined, it is seen that the peaks of the H-0.5 and H-1 membranes are obtained at lower wavenumbers compared to the H-0 membrane, and the peak intensities are higher. On the contrary, it is seen that the peaks of the H-2 and H-3 are obtained at higher wavenumbers, and the peak intensities are lower. From this, it is concluded that the crystallinity of the H-0.5 and H-1 is lower than that of the H-0, the crystallinity of the H-2 and H-3 is higher than that of the H-0, and better conductivity will be obtained if the peak intensity increases.^[30,32,33]

XRD analyses were performed to examine the crystal structures of produced membranes and the obtained XRD diffractograms are presented in Figure 5(b). In the XRD diffractograms, a broad peak attributed to the mixed crystalline and amorphous phases is seen at a refractive angle of $2\theta = 12^\circ - 20^\circ$, and other broad peak can be seen between $2\theta = 30^\circ - 50^\circ$.^[34] The peak which is around 18° is ascribed to the distance between the two polytetrafluoroethylene (PTFE) moieties in the membrane. When more than 1% Al₂O₃ was added to the structure, a sharpening of the peak of the crystal phase and an increase in the peak intensity occurred. Since the increase in peak intensity indicates that the crystallinity increases,^[35] it was concluded that the addition of more than 1% Al₂O₃ to the structure increases the crystallinity. A decrease in peak intensity is observed in Li-0.5 and Li-1 membranes compared to the Li-0 membrane. This situation is likely caused by the interaction of the inorganic nanofiller with the polymer chain, which differs from material to material. In Li-0.5 and Li-1 membranes, Al₂O₃ settled between the Nafion and Aquivion polymer chains, allowing the formation of free volume in the membrane and making the structure amorphous. Excessive reinforcement of nano Al₂O₃ to the structure causes the formation of the regular structure of the polymer nanocomposite and therefore high crystallinity is obtained. This is explained by the interaction of alumina with the polymer group as well as with the polymer surface.^[15,30] The result obtained from the XRD diffractograms also confirms the result obtained from the FTIR spectra. As a result, since the low crystallinity of the ion exchange membrane

is important for the conductivity of the membrane, it is clearly seen that Li-0.5 and Li-1 membranes will provide higher electrochemical capacity by offering higher conductivity.

Membrane morphology

The change in membrane morphology was investigated by FESEM when Al₂O₃ nanofillers were reinforced at different rates into the membrane structure. Surface and cross-section FESEM images of Li-0, Li-0.5, Li-1, Li-2, and Li-3 hybrid composite membranes are shown in Figure S3(a–j). When these images are compared, as the percentage of Al₂O₃ increases, the grain sizes accumulate, and the coarseness of the surface morphology increases. As seen in the surface and cross-sectional images, the Al₂O₃ particles dispersed in the membrane structure show agglomeration, especially in the 3% reinforced structure. This creates an effect that disrupts the membrane structure and prevents ion passage. When the surface and cross-section morphology of 0.5% and 1% Al₂O₃ reinforced structures is examined, it is seen that the nanofiller distribution is more homogeneous, and agglomeration is not observed. From this point of view, 0.5% and 1% Al₂O₃ supplementation provided the desired target morphology in the membrane structure.

Electrochemical characterizations

It is important to measure the membrane's conductivity to determine the membrane's electrochemical behavior in Li–S cell. To this end, EIS measurements were performed for hybrid composite membranes. Based on the resistance values measured here, the membranes' conductivities were calculated according to the formula given by Equation 3.^[18] Each membrane's conductivity is given in Table 6. Based on the results, it was observed that all Al₂O₃ reinforced membranes showed high conductivity values and gave results close to each other. As seen in Table 6, 1% Al₂O₃ reinforced membrane (Li-1) provided the highest conductivity, followed by Li-0.5, Li-2, and Li-3

Membrane	Conductivity (Scm ⁻¹)
Li-0.5	2.32×10 ⁻⁴
Li-1	2.84×10 ⁻⁴
Li-2	1.95×10 ⁻⁴
Li-3	1.83×10 ⁻⁴

membranes. For Li-0.5 and Li-1 membranes, conductivity increased due to the growing amorphousness of the membrane with the increase of Al₂O₃ reinforcement. However, when 2% or more Al₂O₃ is added, the decrease in conductivity has shown that excess Al₂O₃ additive causes a negative effect on the conductivity of the membrane. Also, in the study of Liu et al., it was seen that excessive Al₂O₃ contribution to the Nafion membrane negatively affects conductivity.^[13]

It is important to have information about the electrochemical window of the electrolyte, which is intended to be used in the battery, to understand the practical applicability of this electrolyte in the battery.^[36] The electrochemical stability of the Li-1 membrane was examined via cyclic voltammetry at 25 °C. In Figure 6, the CV curve taken in the potential range of -0.5 to +5.0 V and 0.1 mVs⁻¹ scan rate can be seen.

The peaks of the cathodic and anodic currents, which correspond to the lithium deposition and stripping process, are observed at -0.15 V and +0.30 V, respectively.^[21] Moreover, no current was observed due to electrolyte degradation up to 4.25 V. From this, it was determined that the electrochemical window of the membrane was between about 0 V and 4.25 V. When considered the voltage range applied to the Li-S battery is 1.5–3.0 V, the membrane has sufficient electrochemical stability and is applicable in Li-S battery systems.

Cyclic voltammetry (CV) analysis was performed to determine the voltage values at which electrochemical reactions take place in Li-S battery. The cyclic voltammogram of the cell formed with Li-1 membrane was taken for five cycles at

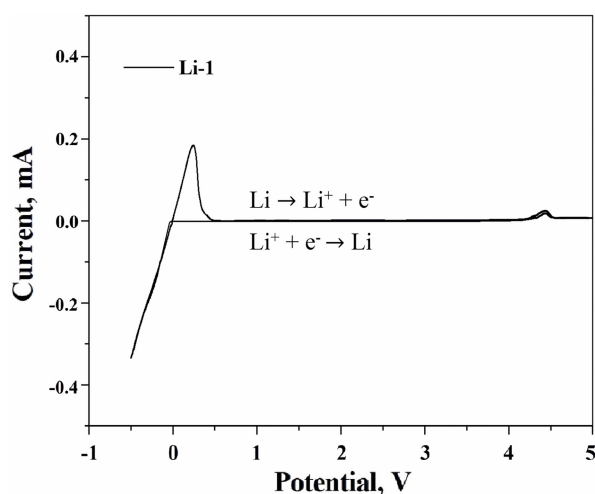


Figure 6. Cyclic curve of the Li-1 membrane taken at a scanning rate of 0.1 mVs⁻¹.

0.1 mVs⁻¹ scan rate at a potential range of 1.5–3.0 V and is presented in Figure 7(a). The electrochemical events occurring in all-solid-state Li-S batteries are known to be different from those containing liquid electrolytes. In the cathodic scan, two reduction peaks of approximately 1.85 V and 2.05 V are observed; the first corresponds to the formation of PS (Li₂S_n, n = 4–8) and the second to the formation of Li₂S₂ and Li₂S. After the second cycle, the overlapping of the CV curves displays that the cycling capability is good.^[37] When the peaks in the anodic region are examined, the first oxidation peak is around 2.5 V and the second oxidation peak is about 2.6 V. While the first peak is ascribed to the formation of Li₂S_n (n > 2) as a result of Li₂S₂ and Li₂S oxidation, the second explains the sulfur (S₈) formation.^[28,38] These oxidation peaks are in the form of a large peak intertwined with each other. However, shifts are observed in the obtained peaks. For example, while reduction peaks are seen at 2.3 and 2.0 V in the CV voltammogram of the conventional Li-S cell, it is seen that these peaks shift to lower voltage values in the Li-S cell formed by the membrane produced in this study. When the liquid electrolyte is used, the polysulfides formed as a result of the related reaction dissolve in the liquid electrolyte and pass through the traditional separator and make shuttle movement. However, polysulfide anions cannot pass from the membrane used as electrolyte in solid state batteries to the anode side. As a result, these polysulfide anions accumulate on the membrane side, causing a reduction potential difference compared to liquid electrolyte batteries.^[39] From this, it is understood that the produced membranes prevent polysulfide migration.

Galvanostatic charge-discharge tests were applied to determine the cycling performances of the membranes in CR2032 type Li-S half-cells formed by using the produced hybrid composite membranes and S/rGO/CNT cathodes. The tests were carried out at a potential range of 1.5–3.0 V, at a speed of 0.1 C, under constant current density. In Figure 7(b), the galvanostatic charge-discharge curves of cells containing Li-0, Li-0.5, Li-1, Li-2, and Li-3 membranes with different Al₂O₃ content are given for the first cycle. From this, it can be seen that the capacity values of cells with hybrid composite membranes are close to each other for the first cycle. In addition, when the plateaus occurring during charging and discharging are examined, it is seen that they are in the same region in accordance with the peaks seen in the CV curves given in Figure 7(a).

The cycling capability of the produced membranes was compared for 300 cycles. In Table 7, the specific discharge capacities and capacity retention values for the first, second, hundredth, and three hundredth cycles for Li-0, Li-0.5, Li-1, Li-2, and Li-3 membranes are given. As seen in Table 7, in the first discharge, 1349, 1356, 1360, 1328, and 1316 mAhg⁻¹, in the second cycle, 1209, 1310, 1357, 1308, and 1296 mAhg⁻¹, in the 100th cycle, 827, 877, 905, 807, and 835 mAhg⁻¹, and in the 300th cycle, 774, 822, 868, 748, and 710 mAhg⁻¹ discharge capacities were obtained from cells with Li-0, Li-0.5, Li-1, Li-2, and Li-3 membranes, respectively. When the results were examined, Li-1 membrane containing 1% Al₂O₃ provided the highest capacity, Li-3 showed the lowest capacity, followed by Li-2, Li-0, and Li-0.5 membranes. When the capacity retentions

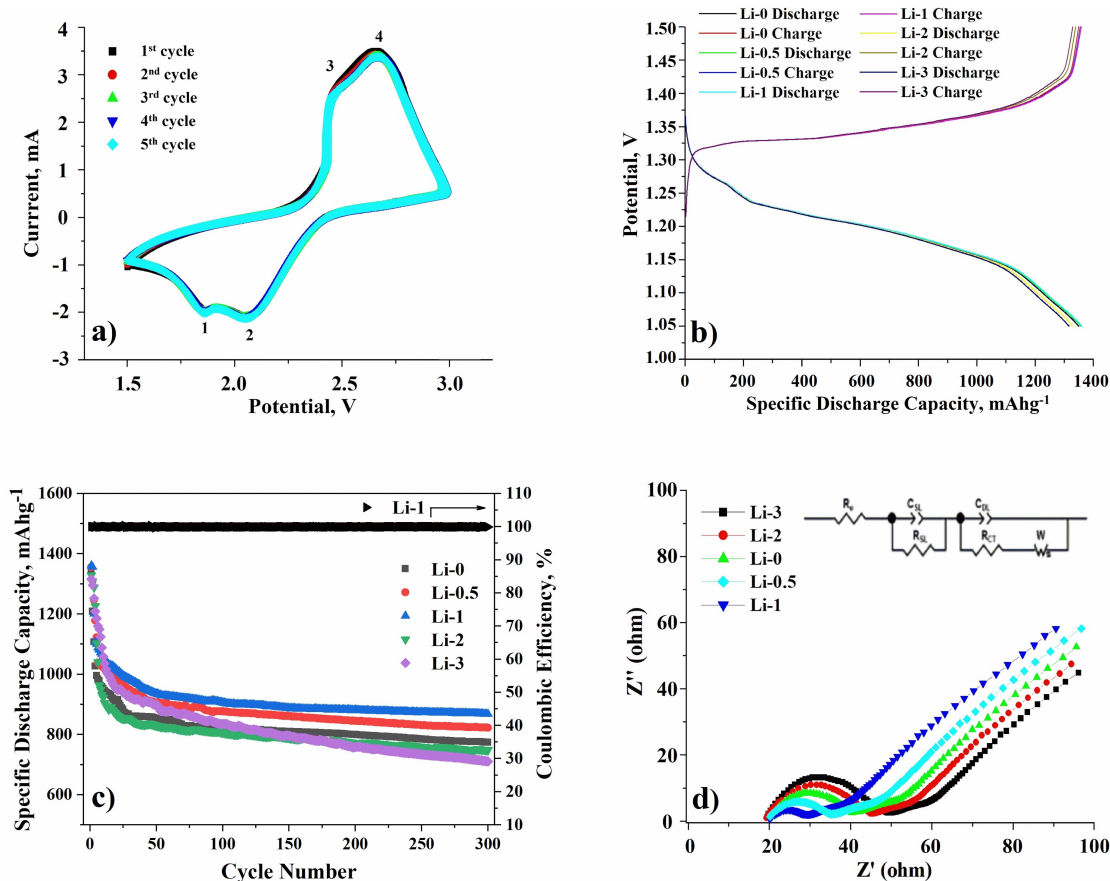


Figure 7. (a) Cyclic voltammogram of the cell with Li-1 hybrid composite membrane at a scanning rate of 0.1 mVs^{-1} ; (b) Galvanostatic charge-discharge voltage curves of Li-0, Li-0.5, Li-1, Li-2 and Li-3 membranes; (c) Cycle capability of Li-0, Li-0.5, Li-1, Li-2 and Li-3 membranes and Coulombic efficiency of Li-1 membrane at 0.1 C over 300 cycles; (d) Nyquist curves from cells with produced membranes after 300 cycles (with an equivalent circuit adapted to Nyquist curves).

Table 7. Discharge capacities and the capacity retention of the cells with produced membranes.

Sample Name	1 th Cycle mAhg^{-1}	2 nd Cycle mAhg^{-1}	100 th Cycle mAhg^{-1}	300 th Cycle mAhg^{-1}	Capacity Retention, %
Li-0	1349	1209	827	774	57.4
Li-0.5	1356	1310	877	822	60.6
Li-1	1360	1357	905	868	63.8
Li-2	1328	1308	807	748	56.3
Li-3	1316	1296	835	710	53.9

are examined, the cell with Li-0 membrane provided 57.4% capacity retention at the end of 300 cycles. In comparison, the Li-1 membrane cell had the highest value with 63.8%, followed by Li-0.5 with 60.6% capacity retention. On the other hand, the cell with Li-3 membrane gave the lowest capacity retention value of 53.9%, followed by Li-2 with 56.3% capacity retention. Compared to the Li-0 membrane, Li-0.5 and Li-1 hybrid composite membranes prevented polysulfide migration more effectively. Due to their high conductivity value provided by their amorphous structure, they showed more effective electro-

chemical stability and increased capacity retention, especially after 50 cycles.

This situation is clearly observed in Figure 7(c), and the charge-discharge capability of Li-0, Li-0.5, Li-1, Li-2, and Li-3 membranes for 300 cycles is compared. Here, Li-1 membrane provided the highest capacity from the first cycle. Li-2 and Li-3 membranes, especially Li-3, showed a faster capacity decrease compared to the Li-0 membrane, while Li-0.5 and Li-1 offered more stable cycling capability. This situation is caused by the Al_2O_3 additive facilitating Li^+ ion transition by increasing the amorphousness of the polymer and thus its conductivity. However, if 2% or more Al_2O_3 is added, the nanofiller accumulates in the spaces of the membrane, blocking the Li^+ ion passageways and increasing the internal resistance, affecting the electrochemical capacity negatively. For this reason, it is clearly seen that it is important to reinforce Al_2O_3 to the membrane at an optimum value. Figure 7(c) also shows Coulombic efficiency of the Li-1 proving its superior cyclability and stable Coulombic efficiency with $\sim 100.0\%$ value even after 300 cycles.

Impedance measurements were carried out after 300 charge-discharge cycles. Nyquist curves of cells assembled with Li-0, Li-0.5, Li-1, Li-2 and Li-3 membranes and equivalent circuit

Table 8. Impedance parameters taken from the cells with produced membranes after 300 cycles.

Sample Name	Rs (ohm)	Rct (ohm)
Li-0	20.7	52.1
Li-0.5	20.2	46.4
Li-1	20.1	39.1
Li-2	19.3	56.9
Li-3	19.5	60.2

of these cells are shown in Figure 7(d). The Nyquist curves of the cells assembled with these membranes consist of two semicircles in the high-frequency region and an inclined line in the low-frequency region, related to the charge-transfer resistance and ion diffusion into the cathode, respectively. Rs and Rct values obtained from fitting these semi-circles to the circuit are given in Table 8. When Table 8 is examined, the fact that the Rct values of the cells assembled with Li-0.5 and Li-1 membranes are smaller than Li-0 shows that the conductivity of the membrane increases when Al₂O₃ is reinforced to the membrane. As a result, based on the Rct value, the cell with Li-1 membrane was the cell with the lowest resistance. In the light of the data obtained, it has been concluded that the point where the Al₂O₃ reinforcement reaches the optimum value in terms of both conductivity and discharge capability is 1% Al₂O₃ reinforced.

Consequently, Al₂O₃ reinforced Li-Naf:Li-Aqu membrane is used to reduce the loss of active material by preventing the passage of polysulfides from the cathode to the anode. While Al₂O₃ was used as an adsorbent to trap polysulfides, Li-Naf:Li-Aqu membrane effectively prevented polysulfide migration, thanks to its properties that allow the migration of Li⁺ cations but obstruct transportation of negatively charged polysulfide anions.

Conclusions

In summary, hybrid composite ion-exchange membranes with lithiated Nafion and lithiated Aquivion based Al₂O₃ nanofiller reinforced have been developed as separator and electrolyte in Li-S batteries. Al₂O₃ nanofiller reinforcement (0.5%, 1%, 2%, 3%) was applied to the 1:2 (Li-Naf:Li-Aqu) composition. As the amount of Al₂O₃ in the hybrid composite membrane increases, the ion exchange capacity and solvent uptake, which can be the conductivity criterion, increase. As a result of the tensile tests, it was observed that the increase in the amount of Al₂O₃ in the membrane increased the elasticity limit and caused an improvement in its mechanical properties. When the ability of the membranes to prevent polysulfide migration was examined, it was seen that the produced membranes could avoid polysulfide migration, unlike the commercial separator. The overlapping of the curves in the cyclic voltammograms taken in the CR2032 type Li-S half-cell showed that the cycling

capability was good, and the reversibility was provided in the charge-discharge reactions. In charge-discharge tests, at the end of 300 cycles, the highest discharge capacity of 868 mAhg⁻¹ was obtained, and the highest capacity preservation was achieved at 63.8% when Li-1 hybrid composite membrane was used. It has been proven that nanofiller reinforcement to ion exchange membrane improves electrochemical stability by reducing polysulfide migration in Li-S batteries. As a result, polysulfide dissolution and the accompanying shuttle effect are prevented by using Al₂O₃ nanofiller reinforced lithiated Nafion and Aquivion ion-exchange membranes instead of traditional organic liquid electrolytes. In this way, both the cathode integrity is preserved, and the anode corrosion is prevented. Thus, Li-S batteries with higher discharge capacity, longer cycle life, and more stability have been developed.

Acknowledgements

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Conflict of Interests

There are no conflicts of interest to declare.

Data Availability Statement

Research data are not shared.

Keywords: Al₂O₃ · Aquivion · Ion exchange electrolyte · Li-S batteries · Nafion

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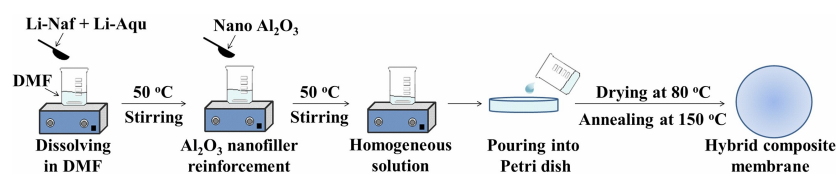
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RESEARCH ARTICLE



Al₂O₃ reinforced Nafion/Aquivion hybrid composite membranes were prepared for Li–S battery applications. Forming a hybrid composite membrane with nano-Al₂O₃ increased the electrochemical capacity. 868 mAhg⁻¹ discharge capacity and

63.8% capacity retention were obtained at the end of 300 cycles. The properties of the Nafion/Aquivion composite membrane have been improved by utilizing nanomaterial reinforcement.

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1 – 11

Nanofiller-Based Novel Hybrid Composite Membranes for High-Capacity Lithium-Sulfur Batteries

