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3D printing of micropatterned anion exchange membranes

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Structured membranes play an important role in improving the flow and resistance characteristics of ion-conducting membranes. Micro-patterned anion exchange membranes have been 3D printed via a photoinitiated free radical polymerization and quaternization process. The photocurable formulation, consisting of diurethane dimethacrylate, poly(ethylene glycol) diacrylate, dipentaerythritol penta-/hexa- acrylate, and 4-vinylbenzyl chloride, was directly cured into patterned films using a custom 3D photolithographic printing process similar to mask projection stereolithography. Measurements of water uptake, permselectivity, and ionic resistance were conducted on the quaternized poly(DU-co-EG-co-VBC) samples to determine their suitability as ion exchange membranes. The water uptake of the materials increased as the ion exchange capacity (IEC) increased due to greater quaternized VBC content. Samples with IECs from 0.98 to 1.63 meq/g were possible with the VBC content ranging from 15 to 25 weight %. The water uptake was sensitive to the amount of PEG in the sample with membranes showing water uptakes from 85 to 410 weight % with PEG fractions from 0 to 60 weight %. The permselectivity of the anion exchange membrane samples decreased from 0.91 (168 weight %, 1.63 meq/g) to 0.85 (410 weight %, 1.63 meq/g) with increasing water uptake and to 0.88 (162 weight %, 0.98 meq/g) with decreasing IEC. These results were relatively consistent with the general view of permselectivity being correlated to the water uptake and ion content of the membranes. Lastly, it was revealed that the ionic resistance of patterned membranes was lower than that of flat membranes at the same material volume. A parallel resistance model was used to explain how the patterning contributed to the overall measured membrane resistance. This model may provide a way to maximize the membrane's performance by optimal patterning on the surface without chemical modifications of the membrane structure.

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