

Formation of a Battery from an Ion-exchange Membrane and a Polypyrrole Composite

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A composite membrane, composed of polypyrrole anisotropically incorporated into an anion exchange membrane, when placed between platinum plates, produced an e.m.f. which changed with relative humidity like a hygrometer; a lithium battery with an e.m.f. of 2.5 V has been obtained by piling up the composite membrane, swollen with propylene carbonate, on lithium foil.

It is well known that aniline, pyrrole, thiophene, and other heterocyclic and aromatic compounds may be polymerized to give conducting polymers by electrochemical oxidation¹ or using oxidizing agents such as iron(III) chloride,² potassium persulphate,³ etc.⁴ However, in order to improve their mechanical properties, processibility, and atmospheric stability, polymer-polymer composites have been studied,⁵⁻⁸ and the application of polyaniline, polypyrrole, polythiophene, and so on, in batteries has recently been studied.⁹⁻¹² These p-type conducting polymers are one kind of anion exchangeable material with accompanying electron transfer. It is interesting to examine properties of composite membranes composed of conventional anion exchange membranes and p-type conducting polymers.

In this work, commercial anion exchange membranes, NEOSEPTA AM-1 (thickness 0.013 cm, anion exchange capacity 1.96 meq./g dry membrane, strongly basic) and

NEOSEPTA AFN (thickness 0.015 cm, anion exchange capacity 3.03 meq./g dry membrane, strongly basic) (Tokuyama Soda Co. Ltd.) were used as anion exchange membranes. Pyrrole was easily adsorbed into these membranes. The composite membranes were then made as follows. An aqueous pyrrole solution (5%) was held in contact with one side of the membrane for 24 h using an appropriate two-compartment cell, and then this side was brought into contact with an aqueous solution of iron(III) chloride (3%) for 4 h to polymerize the membrane-adsorbed pyrrole. The resultant composite membrane had an anisotropic structure and properties: one side was not conducting (the side which had not been in contact with pyrrole solution) and the other was highly conducting (the composite layer of polypyrrole and the anion exchange membrane matrix) in the dry state.

Figure 1 shows the result of X-ray micro-analysis of a cross-section of the composite membrane after immersion in

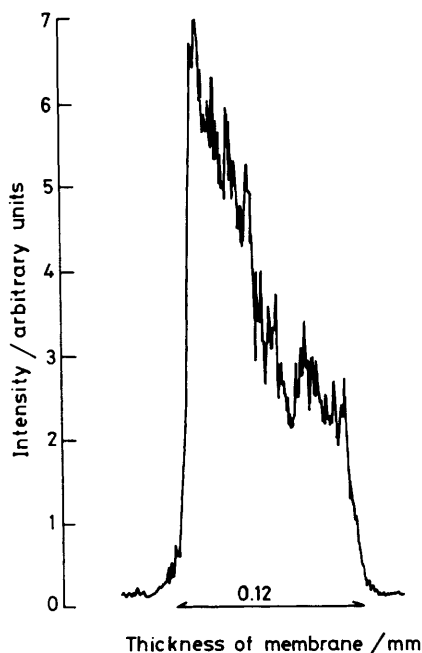


Figure 1. X-Ray micro-analysis of a cross-section of a composite membrane (NEOSEPTA AM-1 and polypyrrole) equilibrated with acidic Na_2WO_4 solution.

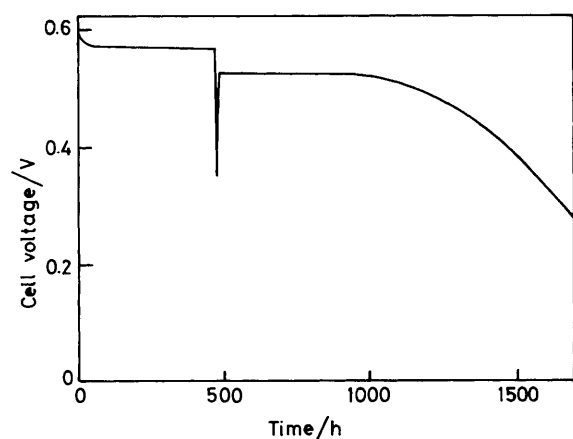


Figure 2. Change in e.m.f. of a composite membrane (NEOSEPTA AM-1 and polypyrrole) with time.

an acidic aqueous solution of Na_2WO_4 (WO_4^{2-} was ion-exchanged and doped). Polypyrrole exists only on one side of the membrane. Even if pyrrole was adsorbed into the inner part of the membrane, it is thought that pyrrole is protonated on contact with the acidic aqueous iron(III) chloride solution, excluded on the surface of the anion exchange membrane by Donnan Exclusion, and polymerized on the surface of the membrane.

Figure 2 shows the change in e.m.f. of the dry composite membrane (NEOSEPTA AM-1), tightly held between two platinum plates (membrane area 1.0 cm^2). An e.m.f. of $0.5\text{--}0.6 \text{ V}$ was maintained for 40 days and then decreased gradually. A current of $0.25\text{--}0.30 \mu\text{A}$ was discharged because the load resistance was $2.0 \text{ M}\Omega$. The relative humidity in the measuring atmosphere was $55\text{--}60\%$. When the relative humidity decreased to about 40% at 480 h, the e.m.f. decreased abruptly. It increased again rapidly with increasing

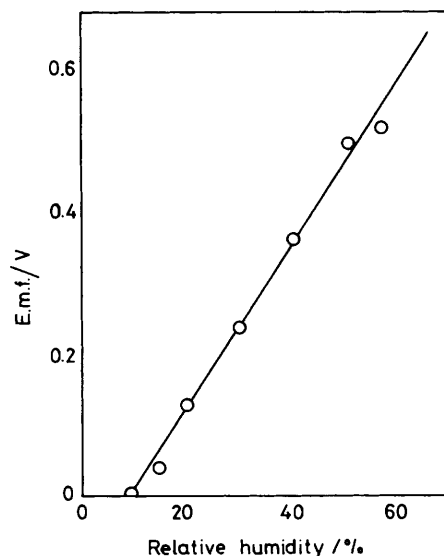


Figure 3. Relationship between e.m.f. and relative humidity for a composite membrane composed of NEOSEPTA AM-1 and polypyrrole.

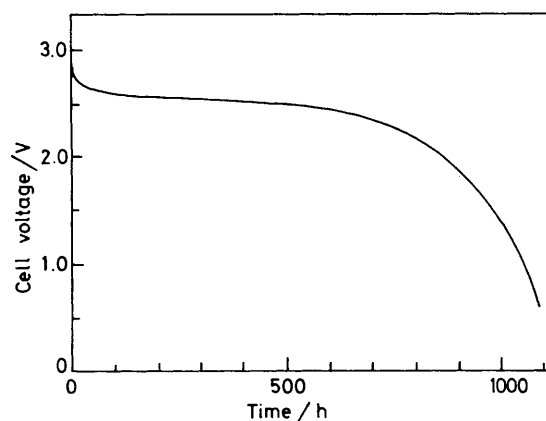


Figure 4. Discharge curve for a Li-composite membrane battery, using a composite membrane composed of NEOSEPTA AFN and polypyrrole, with a load resistance of $2 \text{ M}\Omega$.

relative humidity, but did not attain the same value in this composite membrane. Figure 3 shows the relationship between e.m.f. and relative humidity, measured for another composite membrane. The e.m.f. decreased linearly with decreasing relative humidity and this relationship was fairly reversible. The composite membrane shows the properties required of a hygrometer.¹³ This means that the composite layer of anion exchange membrane matrix and polypyrrole behaves like the anode material of a battery and the thin anion exchange membrane layer as an electrolyte layer. Chloride ions which migrate through the anion exchange membrane layer would discharge on the platinum plate ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$). Migration of chloride ions becomes difficult, so that e.m.f. decreases, when the water content of the anion exchange membrane layer decreases.

In order to prove this deduction, a composite membrane in which polypyrrole had been incorporated from both sides of

NEOSEPTA AM-1 was immersed in an aqueous solution (5%) of pyrrole for 24 h and then immersed in aqueous iron(III) chloride solution (3%) for 4 h. This composite membrane showed no e.m.f. when placed between platinum plates, or even using Al, Zn, or Li foils. Undoping of the membrane by immersion into 0.5 M aqueous ammonia solution still did not produce an e.m.f.

A composite membrane composed of NEOSEPTA AFN (high ion exchange capacity) and polypyrrole was piled up on lithium foil after the composite membrane had been dried under vacuum, the side of the anion exchange membrane layer being in contact with lithium foil. The e.m.f., measured by high impedance volt-meter (impedance $10^{11} \Omega$), was 3.0 V. However, the e.m.f. of the composite decreased below 1.0 V within 24 h, though it was slightly dependent on the anisotropy caused by the presence of polypyrrole. Therefore, the composite membrane was swollen with propylene carbonate after drying under vacuum and then piled up on lithium foil. Figure 4 shows the discharge behaviour with a load resistance of 2 M Ω . A cell voltage of >2.5 V was maintained for about 600 h. The chloride ion content of NEOSEPTA AFN increased from 3.03 meq./g dry membrane to 3.45 meq./g dry membrane by incorporation of polypyrrole into the membrane (determined by ion chromatography after elution of Cl⁻ using tetramethylammonium ions). The ratio of discharged equivalent of chloride ions to those contained in the composite membrane was about 40%. It is understood from this result that not only chloride ions doped with

polypyrrole, but also those ion-exchanged with anion exchange groups are discharged.

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