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Protein pump provides proton power

Bacteriorhodopsin, a natural proton-pumping protein, has been engineered into a polymer membrane that can reverse the problem of proton leakage within fuel cells.

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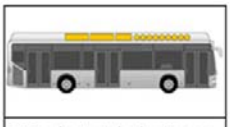

Using bacteriorhodopsin as a proton-exchange membrane may help to make future hydrogen-powered buses more efficient by reducing proton leakage. Image © Ballard Power Systems.

The performance of fuel cells might be improved by a nano-engineered membrane containing light-activated protein pumps. Carlo Montemagno and co-workers at the University of California at Los Angeles have shown[1] that these proteins can reduce leakage of ions across the two chambers of the cell.

Montemagno's team has made polymer membranes studded with the proton-pumping bacterial protein bacteriorhodopsin (bR). They have laminated these films to the proton-exchange membranes of methanol fuel cells. This membrane, generally made from the sulphonated fluoropolymer Nafion, transports protons between the two half-cells of the device, completing the electrochemical circuit. But proton leakage in the 'wrong' direction reduces the overall efficiency of the fuel cell.

With the bR layer attached, however, the hybrid proton-exchange membrane has lower proton leakage, because protons lost in the wrong direction can be pumped back into the Nafion film by bR, when it is illuminated with green light.

The key is to find a way of incorporating bR into a robust synthetic membrane without the protein losing its function. This degradation could happen, for example, if the bR were to partially unfold when removed from its natural environment in the so-called 'purple membrane' of the bacteria *Halobacterium halobium*, a species that thrives in salt marshes.

Montemagno's group has been working for some time to develop a system that will host membrane proteins in a stable, biomimetic matrix. As well as creating proton-pumping films from bR, he is looking to use redox proteins such as cytochrome c oxidase to enhance electron transport, and the water-transporting protein aquaporin to create water-purification filters.

The researchers find that the environment in the lipid bilayers of natural cells can be mimicked using block copolymers of the form ABA, where the A blocks are hydrophilic and the B blocks hydrophobic. The block copolymer molecules can be organized into films just one molecule thick, and a few nanometres wide, using the Langmuir–Blodgett method of floating the molecules on the surface of a solvent and compressing the floating layer with a moveable bar.

These films have an ABA sandwich structure that reflects that of the constituent polymer molecules. Montemagno and colleagues terminate one end of the polymer chains with methacrylate groups, which can be crosslinked to form a robust film.

Membrane proteins such as bR can be incorporated into these copolymer membranes by adding the proteins (solubilized with surfactants) to the mixture in the Langmuir–Blodgett trough. The polymer films sufficiently resemble the hydrophilic–hydrophobic–hydrophilic structure of natural cell membranes to enable their embedded proteins to be kept 'active'.

Bacteriorhodopsin pumps protons preferentially from inside to outside the bacterial cells, driven by a change in protein conformation due to photoisomerization of a chromophore within the molecule. If this unidirectional pumping mechanism is to be used in the synthetic polymer membrane, the bR molecules must be oriented all in the same direction. To do this, the researchers tag the 'extracellular' side of the bR with a small molecule called biotin, which will plug into a protein called streptavidin coating the surface of a substrate to which the polymer monolayer is then transferred.

For example, to make a Nafion membrane backed with the nanoscale-thickness polymer–bR film, the researchers first coat the Nafion with a very thin layer of gold, which they coat in turn with streptavidin. When this membrane is then dipped, gold side first, into a Langmuir–Blodgett trough containing the polymer–bR layer, it emerges coated with a film in which all the bR molecules face the same way.

Montemagno and colleagues find that this composite membrane allows a higher rate of proton transport from a low-pH to a high-pH solution on either side, relative to bare Nafion, when it is illuminated with green light. This is because the osmotic flow of protons through the Nafion down the concentration gradient is enhanced by active pumping through bR. (The gold adhesion layer is thin enough to be highly porous, so it doesn't impede this flow.)

Better still, when the orientation of the membrane is reversed, the equalization of pH is slowed down, because the bR proteins oppose osmotic proton transport by pumping them back in the other direction. Indeed, the composite film is able to maintain a more or less stable pH imbalance across its two sides for long periods.

In a fuel cell, hydrogen at one electrode donates electrons and forms hydrogen ions (protons), while oxygen at the other electrode takes up electrons and forms hydroxide. The flow of electrons between the electrodes is balanced by the flow of protons through the proton-exchange membrane from the hydrogen to the oxygen half-cell. But proton leakage in the reverse direction compromises this process. Montemagno and colleagues estimate that their composite Nafion/polymer-bR membranes could counteract a proton leakage of up to 8 per cent.

References

1. Ho D., Chu B., Lee H. & Montemagno C. D. Protein-driven energy transduction across polymeric biomembranes. *Nanotechnology* **15,** 1084–1094 (2004) Article