A Reference Electrode Based on a Microfluidic-Flowing Liquid Junction Through a Nanochannel Glass Array

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Using an innovative combination of microfluidics and glass nanochannels, an exceptionally stable and long-lived reference electrode has been developed. It uses a microfluidic-flowing liquid junction (MLJ) through a nanochannel glass (NCG) array. The combination allows independent control of electrolyte flow volume, electrolyte flow velocity, and electrolytic resistance. This paper presents data on the performance of the MLJ reference electrode system in a variety of environments.

Precision measurement of pH, Na+, Ca+, and many other ions using selective electrodes requires a stable and reliable reference electrode. For practical use in monitoring industrial processes long-lived reference electrodes with low maintenance are desired. Industrial processes operating at high pressures also require prevention of forced back flow of sample into the electrode's electrolyte.

The measured potential of a reference electrode depends on the stability of the liquid junction potential. The most stable, reproducible, and reliable reference electrodes use flowing liquid junctions, with quartz fiber electrodes preferred for precision measurements. However, flowing liquid junction electrodes introduce a significant amount of contaminants into the sample, are sensitive to high pressures, and need considerable maintenance, which makes them impractical for most industrial applications. Therefore, gel-filled reference electrodes, using a diffusion liquid junction, dominate the industrial market despite their slow response and severe drifting.

Fabrication of NCG arrays used in MLJ electrodes uses a process developed by the Naval Research Laboratory (NRL) that produces arrays with regular cylindrical channels, uniform channel size, and an ordered distribution of channels (Fig. 1). Glass has the mechanical strength, chemical inertness, and high melting point needed for widespread commercial use. The typical NCG used for MLJ reference electrodes has 100 to 1000 channels with a 100 to 800 nm channel ID. By pneumatically pressurizing a collapsible bladder, used as the electrolyte reservoir, a microfluidic-flowing liquid junction is formed with an electrolyte flow rate ≥ 1 µl/hr.

This extremely low flow rate leads to long life, low maintenance, and low sample contamination. A prototype pH sensor employing an MLJ reference electrode (Fig. 2) was tested in solutions covering a wide range of ionic strength and pH, including deionized (DI) water, 0.1 M HCl, and 0.1 M NaOH. Fig. 3 compares the rate of recovery of quartz fiber, gel-filled, and MLJ reference electrodes to their original potential after exposure to 0.1 M NaOH for 3 hours. Fig. 4 compares the response time of these electrodes in a variety of solutions. Sensors with MLJ and quartz fiber electrodes responded rapidly to pH change. Sensors using gel-filled electrodes lagged behind and had a significant pH value offset. These results indicate that the MLJ reference electrode has a rapid recovery (< 5 sec) to its original value, drifts < 0.06 mV/hour, and is able to maintain a stable flow rate over a two-month testing period.

The MLJ reference electrode, because of its low maintenance, fast response, and long-life, will find wide application in precision potentiometric measurement, on-line monitoring, and instrumentation (e.g., blood gas analyzer).

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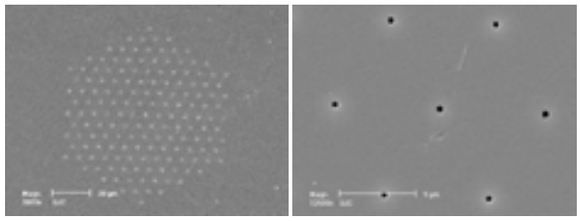

Fig. 1: SEM images of an NCG wafer.

Fig. 2: Photograph of an MLJ pH sensor.

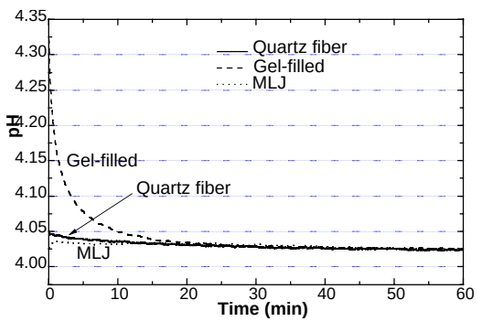

Fig. 3: MLJ and quartz fiber reference electrodes returned to their original potential after exposure to 0.1 M NaOH, while the gel-filled reference electrode lagged behind.

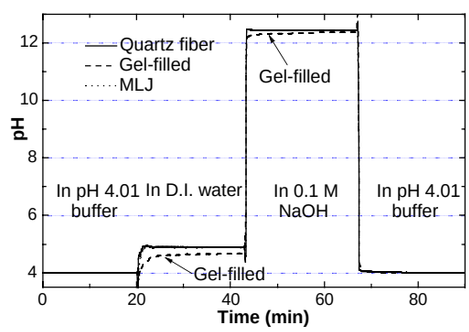

Fig. 4: Response of MLJ, quartz fiber, and gel filled reference electrodes to pH change. The gel-filled electrode lagged behind and was offset.