SOLVING THE LIQUID-JUNCTION POTENTIAL PROBLEM FOR REFERENCE ELECTRODES

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This paper describes an innovative reference electrode that improves the accuracy and operational life of potentiometric sensors. Taking advantage of recent developments in microfluidics and nanotechnology, a novel microfluidic flowing-liquid junction (MLJ) reference electrode has been developed that exhibits a practically invariant liquid-junction potential. The liquid junction is formed at the interface of the reference electrode and the sample solution. The liquid-junction potential results from differences in ionic composition between the reference electrolyte and the sample solution. The MLJ reference electrode helps maintain a constant solution composition at the liquid junction, resulting in a constant liquid-junction potential, which significantly increases the precision of potentiometric measurements and sharply reduces the need for frequent sensor recalibration. This greatly improves the utility of pH sensors for use over prolonged periods of time and in remote locations. In addition, the MLJ reference electrode is compatible with all conventional potentiometric sensors and instrumentation.

There have been numerous studies pertaining to the magnitude and stability of the liquid-junction potential (1)-(3). The accuracy of potentiometric measurements depends on the constancy of the reference electrode potential, including the liquid-junction potential. The requirements to establish a stable liquid junction are well known and documented but until now there has not been a practical solution. The key in solving this problem is to control the interface or liquid junction between the reference electrode and the sample solution.

The liquid-junction potential is controlled by flowing the reference electrolyte through an array of nanochannels at a sufficiently high linear velocity. The nanochannel array provides the means of limiting the volume of electrolyte flow while maintaining a high linear velocity of electrolyte through the nanochannels. The high linear velocity electrolyte through the nanochannel array protects the reference electrode from fouling and prevents back diffusion of the sample solution while limiting volumetric flow rates to less than 1 µl per hour.

Data will be presented comparing the MLJ reference electrode with conventional reference electrodes in a variety of environments. In all of the tests the MLJ reference electrode exhibited a practically invariant reference potential. The MLJ reference electrode potential varied less than 0.5 mV over an 8-hour period with response times less than 60 seconds compared to conventional reference electrode potential variations up to 20 mV and response times of over an hour.

MLJ reference electrodes in industrial process applications could reduce sensor calibration and replacement costs ca. $240 million per year. In addition, this reference electrode can serve as a basic building block for microfluidic devices, an industry projected to approach several billion dollars this decade.

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