**Next-Generation Reference Electrodes with High Potential Stability towards Long-term Sensor Measurements**

Potentiometry provides a simple but powerful platform technology to determine the concentration of specific ion species in solutions and thus has been used in a wide range of applications such as industrial process control, biomedicine, agriculture, and environmental monitoring. However, the potential stability of the reference electrodes (REs) of potentiometric sensors needs to be improved for practical long-term measurement. Further improvement of their ability to counter the influences of interfering ions, pH and temperature variations are also required. Therefore, this thesis is focused on the development of several novel REs through design innovations in materials, structures, and fabrications towards the realization of next-generation potentiometric sensors.

Firstly, we developed a microfluidic channel-based reference electrode (µcRE) consisting of a silver-silver chloride (Ag/AgCl) electrode embedded into a serpentine microfluidic channel, and a polymer-based porous fritz that separates the microfluidic channel from an external test cell. Due to an increased length between the Ag/AgCl electrode and the test cell, the rate of changing the concentration of chloride ion at the Ag/AgCl surface due to redox reaction is significantly reduced. The µcRE exhibited a drift rate of -37 µV/hr with only minor responses to environmental temperature and pH. The µcRE was integrated into an extended gate field-effect transistor (EGFET) to realize a potentiometric nitrate sensor that offered a sensitivity of -202.16±5.55 mV/decade to variations in nitrate concentration with 0.997 R-Squared value to its linear fitting. Secondly, we investigated a unique frit-less µcRE using an ultrasmall orifice at the exit of microfluidic channel as a virtual frit. The size reduction of the orifice size helped to decrease the rate of chloride loss from an embedded Ag/AgCl electrode to the external environment, thus increasing potential stability of the reference electrode. Soft lithography technique was employed to form a 10 µm (width) × 50 µm (height) × 1 mm (length) microchannel integrated with a miniature potassium chloride reservoir. Similar to the frit-based µcRE, this frit-less reference electrode is little influenced by variations in temperature and pH and provides comparable performances with traditional bulky and expensive glass-body Ag/AgCl REs for potentiometric measurement. Thirdly, we developed a planar refillable RE with double junctions that could further stabilize the reference potential of potentiometric sensors. The novel planar configuration of the double junctions, in conjunction with screen-printing and 3D printing technologies, allows both potential stabilization and electrode miniaturization. Magnets-assisted sealing allowed flexible replacing and refilling of the internal gels in the reference electrode chambers. The planar double-junction Ag/AgCl RE exhibited practical independence of chloride concentration, and high potential stability over a wide range of both temperature and pH. A drift rate of 75 µV/hr was obtained and a high linearity with 0.999 R-Squared value was demonstrated during potentiometric measurement of nitrate. Lastly, we developed a sandwiched all-solid-state Ag/AgCl RE (S3RE) on a silicon wafer by using standard thick-film processing technique. The S3RE was formed by drop casting a mixture of polyvinyl butyral (PVB) and KCl as the ion-electron transductor and another layer of aromatic polyurethane (PU) as the protection layer by an automated fluid dispensing robot. The presented S3RE showed a comparable performance with the traditional liquid-state REs, in terms of stability, chloride and pH susceptibility, and temperature. We demonstrated all-solid-state ion-selective electrode sensors using S3RE as their reference electrodes for continuous monitoring of nitrate in both soils and plants.