Polyelectrolytes are polymers carrying ionic and/or ionizable groups. Compared with neutral hydrogels, polyelectrolyte hydrogels have many unique properties, such as high water-absorbing capacity, ion exchange ability, ionic conductivity, ion-strength sensitivity, mechano-electrical effect, and very low surface friction. Among them, the electric potential of polyelectrolyte hydrogels is the main physical parameter to dominate their properties. However, little knowledge of electric potential in polyelectrolyte hydrogels is reported in previous study. The difficulties to detect electric potential are: (1) solid-like property of hydrogel; (2) poor contact for traditional detector; (3) complex structure of polyelectrolyte hydrogel. In this thesis, we try to establish a microelectrode technique to detect the electric potential of polyelectrolyte hydrogels. And the measured hydrogels are divided into two types, brittle and ductile hydrogels. Based on this technique, we systematically and quantitatively study how to detect the electric potential of both brittle and ductile hydrogels, and the internal structure of those hydrogels are also declared.

Firstly, we report, for the first time, the quantitative measurement of the local electric potential of brittle polyelectrolyte hydrogels using the microelectrode technique (MET). Given the solid-like nature of the hydrogels, the difficulty of applying MET is how to make a good contact of the microelectrode to the hydrogel. Poor local contact substantial underestimates the potential. We observed that, the potential measured decays exponentially with the increase of capillary diameter of the microelectrode. This behavior is related to the capillary wall thickness that determines the contact distance of the electrode probe to the hydrogel. The characteristic decay length in respective to the wall thickness is very close to the local Debye length around the capillary. The latter is much larger than that of the bath solution due to the reverse osmosis effect. By using microelectrodes with a tip wall thickness less than the local Debye length, the Donnan potential of polyelectrolyte gel could be accurately measured. Using a micromanipulator, the inserting process of the microelectrode is precisely controlled, and the depth profile of electric potential in the hydrogels can be measured with a spatial resolution down to ~5 nm.

Secondly, we try to investigate the counter-ions condensation of polyelectrolyte hydrogels. To measure the activity coefficient of counter-ions in polyelectrolyte hydrogels, we adopt microelectrode technique (MET) to study the potential of polyelectrolyte hydrogels according to Donnan equilibrium. Meanwhile, by confining the swelling of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) networks in the poly(acrylamide) (PAAm) networks, the effect of polymer strands conformation on condensation of counter-ions is also investigated. The results show that the condensation of counter-ions is affected by the conformation of polymer strands: the less stretched polymer strands has more mobile counter-ions and more counter-ions are condensed around the highly stretched strands. We also compared the condensation effect with the linear polyelectrolytes.

Thirdly, we adopt microelectrode to study the electric potential of ductile hydrogel, DN hydrogel. Difference to the brittle polyelectrolyte hydrogel, DN hydrogel is a ductile material that has a small or no crack during the insertion of microelectrode. Due to the elastic behavior of DN gel, the electric potential is independent to the inserting speed of microelectrode. Particularly, the electric potential of DN gel is almost invariable to the diameter of microelectrode at large diameter. However, the electric
potential seems to correspond to the diameter other than wall thickness of microelectrode. A crack blunting model is proposed to explain this phenomenon. The local shrink of clusters may be the main reason to affect the potential value at small diameter. The measured potential of DN gel by using large diameter of microelectrode are considered as as the real Donnan potential of hydrogel, which is correspond to the ideal potential value. Thus, we expect that the potential of polyelectrolyte hydrogel can be accurately measured by using ductile hydrogel, the crack advancing in polyelectrolyte gel can be ignored if we can prepare hydrogel based on DN concept.

Fourthly, we adopt MET to observe the potential of pre-stretched DN hydrogels and study the charge distribution on damage surface. In the tensile test, this technique shows that the link between the potential and fracture of PAMPS networks has a strong relativity. Unlike previous studies, potential curves represent the internal structure of PAMPS networks are also fractured in the necking zone. Meanwhile, this technique is useful to study the damaged surfaces for not only cutting but also tearing DN gels. The thickness of nonuniform surfaces, which are showed on potential curves, is easily overestimated by microscope for tore DN gels.

Lastly, we use MET to study the various polyelectrolyte hydrogels and their internal structure of polyelectrolyte hydrogels. From the spatial distribution of potential, the microstructure of hydrogels both in bulk and near the surface, the thickness of ultrathin hydrogels, and the heterogeneous layered structure of composite gels, can be determined accurately. The MET established in this work provides a powerful tool for direct characterization of the spatial distribution of electric potential of hydrogels.

Above all, MET is useful to quantitatively detect the electric potential of polyelectrolyte hydrogels, not only the brittle hydrogels but ductile hydrogels. In future, it may therefore be considered a valuable tool in observation of potential of various polyelectrolyte gels, such as gradient polyelectrolyte layer, medical release system, response in environments, and fracture mechanism of polyelectrolyte hydrogels.