Electrochemical Impedance Spectra of Hybrid Electrolyte for Energy Conversion

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With the emerging of the concept of hybrid electrolytes recently, the hybrid electrolytes here means a combination of aqueous/solid/non-aqueous electrolytes, its advantages have been exploited to promote the performance of several lithium batteries[1,2]. However, of these usages of hybrid electrolytes, one electrode of batteries was unexceptionally fixed to being metal lithium; thus its application was largely restricted. And it's difficult to quantify to what extent this combinations of electrolyte will affect the energy storages.

Of the batteries that employ aqueous liquid electrolytes, such as Ni–MH, Ni–Cd, Ag–Zn, Pb–acid batteries, has potential windows that are limited to within the range of hydrogen evolution potential to oxygen evolution potential. Organic electrolyte that LIBs employ provides a stable potential range (from 0.0 to 4.5 V vs. Li/Li^+).[3] For solid electrolytes, all solid-state LIBs and Na–S batteries use lithium superionic conductor glass film (LISICON) and sodium super-ionic conductor glass film (NASICON) electrodes, respectively.[4,5] It's apparent that the electrolytes must be stable, with both the anodic and cathodic active materials remaining at their redox electrode potentials.

Based on previous knowledge of hybrid electrolyte, we intend to incorporate one aqueous LiOH solution and one organic ($LiPF_6$+PC), as well as a super Li^+ conductive solid electrolyte (LISICON) into one capacitor. The main objective for this design is to finally achieve a complement between energy density and power density of the device. The base knowledge about this is the fact that fast charge transfer and narrow working potential about 1.2V for aqueous electrolytes, whereas wide working potential windows (normally 2.7V) and slow charge transfer for organic electrolytes. The combination of aqueous and organic electrolyte separated by LISICON will take advantage of merit of each electrolyte; therefore, it is expected that an ideal complement between energy and power density could be performed.

In this study, to identify the specific impedance characteristics for specific aqueous and non-aqueous electrolytes, it's necessary to conduct electrochemical impedance spectra experimental to fix a single electrolyte impedance behavior. Here, the impedance experiments were performed using two-electrode configuration in which two similar Pt plane electrodes were used as working electrode and counter electrode (Fig.1). LiOH solution and $LiPF_6$ solved in PC were used as aqueous and organic electrolyte, respectively, and separated by a super Li^+ conductive solid electrolyte (LISICON).

Fig.2 is the EIS taken at various useful configurations for hybrid electrolyte combinations. The frequency value at low frequency point is considered normally as an indication at which values near phase angle 90^0 mean the electrochemical behaviors more like a capacitive. From the high frequency intercept obtained in EIS, the resistance of electrolyte solution between two Pt electrodes is 20Ω, 200Ω and 350Ω, respectively, for Pt/LiOH/LISCON/LiOH/Pt, Pt/LiOH/LISCON/(PC+$LiPF_6$)/Pt,Pt/(PC+$LiPF_6$)/LISCON/(PC+$LiPF_6$)/Pt three configurations. It's thus determined that the resistance of electrolyte solution of the combination of aqueous, organic and solid electrolytes is between that of aqueous and organic electrolyte. Therefore, such combination of electrolyte will take advantage of the merit of quick charge transfer of aqueous electrolyte, and wide stable operation potential range of organic electrolyte. The energy storage of utilization of this hybrid electrolyte will cause a complement between energy density and power density. The effect of concentration of electrolyte (aqueous or/and organic) on the EIS is underway in our lab and will be published in other journal.

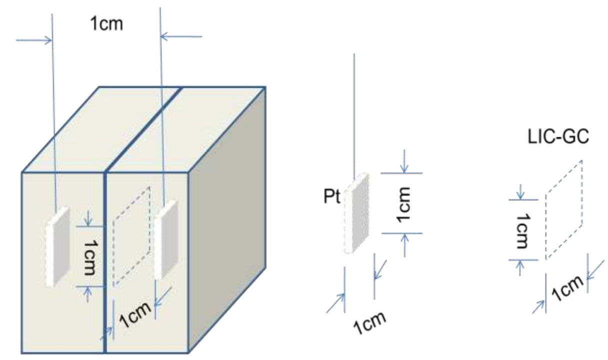

Fig.1. Experimental cell configuration for electrochemical impedance spectra of hybrid electrolytes

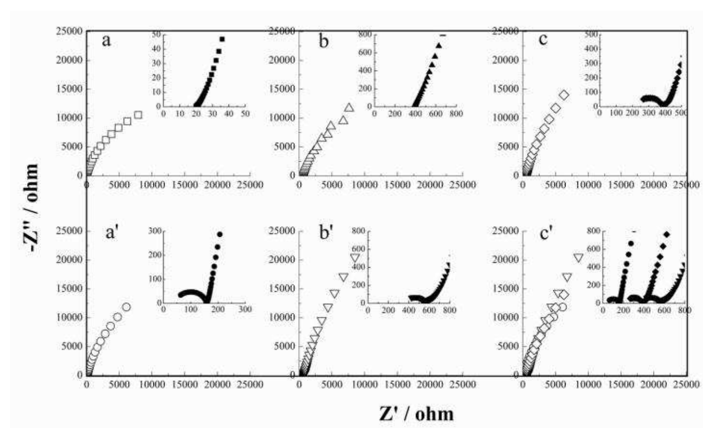

Fig.2. Electrochemical impedance spectra for test cell, (a, a′) Pt/LiOH/Pt, Pt/LiOH/LISCON/LiOH/Pt;(b, b′) Pt/(PC+$LiPF_6$)/Pt,Pt/(PC+$LiPF_6$)/LISCON/(PC+$LiPF_6$)/Pt; (c, c′) Pt/LiOH/LISCON/(PC+$LiPF_6$)/Pt, three cases overlaped.

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