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Impedance Study of Electrochemical Stability Limits for Electrolytes

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Aiming to accurately determine electrochemical stability for electrolytes with electrode of a high surface area in electrochemical capacitors, an impedance method is proposed based on the facts that the phase angle of the impedance curve will decrease as the frequency tends to zero as there electrolyte decomposition occurs. Using the new approach, reliable stability data are obtained for the description of aqueous electrolytes operating in electrochemical capacitors. This new method can also be used to evaluate electrolyte stability in more general systems in which the electrode has a high surface area and reversible faradaic reaction.

Keywords: Electrochemical stability; Impedance; Electrolyte

1. INTRODUCTION

Electrolyte stability measures the ability of its components (solvents and salts dissolved therein) to resist oxidative and reductive decomposition on the charged surface of electrodes. In most cases, the bulk electrolyte in an electrochemical device is expected to remain inert as the desired redox processes are in progress. Therefore its stability is an important parameter that sets the maximum potential limits for device operation. Technically this stability is quantified in terms of a potential range, within which both oxidative and reductive decompositions of the electrolyte are negligible. Conventional practice to determine this potential range has always been based on the i–V polarization curve generated by voltammetry on non-porous working electrodes, such as platinum (Pt) and glassy carbon (GC) [1, 2]. Usually, the selection of the current cut-off criteria carries no theoretical significance and is therefore completely arbitrary. To electrode has a high surface area, the apparent current density corresponding to electrolyte decomposition is much larger than that at the non-porous working electrodes. Moreover, the capacitive current density is often dominant the observed current density, and it is difficult to distinguish non-Faradaic (or capacitive) and Faradaic components on the working electrode [3]. An improved quantification of electrochemical stability limits is proposed by Kang Xu, et al [4], Faradaic and capacitive current can be distinguished by using cyclic voltammetry with continuous extended potential limit (anodic and cathodic territory, separately) when assuming electrolyte decomposition process as irreversible Faradaic process. This method has some advantages over the conventional approach, but needs more complicated data treatment. Furthermore, the assumptions of this method are not always true in actual electrode with a high surface area.

We know that, the electrolyte decomposition process mostly is irreversible Faradaic process with new phase coming forth; the polarization resistance of new phase coming forth measured by impedance has a distinct characteristic of decrease with the frequency decrease in low frequency band [5]. With this perspective, we propose an impedance method to determine the electrolyte decomposition.

2. EXPERIMENTAL

KOH of analytical grade purity and distilled water were used. The electrolyte used was a 7 mol·L^{-1} KOH aqueous solution. All electrochemical measurements were carried out using a Solartron 1280Z workstation in a three-electrode configuration assembly consisting of activated carbon as the counter electrode, Hg/HgO (7 mol·L^{-1} KOH aqueous electrolyte) as the reference electrode. The working electrodes were activated carbon electrodes and NiO_x electrodes, made as described in literatures [6] and [7], respectively. Graphite electrodes (graphite rod embedded in epoxy resin, the circular surface area is about 0.24 cm^2) were used as comparison.

3. RESULTS AND DISCUSSION

Potentiodynamic experiment curve of graphite electrode in 7 mol·L^{-1} KOH aqueous solutions at a scan rate of 10mV·s^{-1} is shown in Fig. 1. As shown in Fig. 1, the anodic (oxidative) and cathodic (reductive) limits of the stability range are assigned as the potentials where the current density reaches a pre-selected level (0.1 or 0.2 mA·cm^{-2} used in this example), e.g., the oxygen generating will be occur at the potential of 0.6V vs. Hg/HgO (cut-off current density is 0.1 mA·cm^{-2}) or 0.75V vs. Hg/HgO (cut-off current density is 0.2 mA·cm^{-2}), and the hydrogen generating will be occur at the potential of -1.15V vs. Hg/HgO (cut-off current density is 0.1 mA·cm^{-2}) or -1.30V vs. Hg/HgO (cut-off current density is 0.2 mA·cm^{-2}). So the electrochemical stability limits for 7 mol·L^{-1} KOH electrolyte on graphite electrode is about 1.75V or 2.05V when the cut-off current density is 0.1 mA·cm^{-2} or 0.2 mA·cm^{-2}. It should be noted that the selection of the current cut-off criteria carries no theoretical significance and is therefore completely arbitrary. Results of potentiodynamic experiment on glassy carbon electrode are similar as those on graphite electrode.

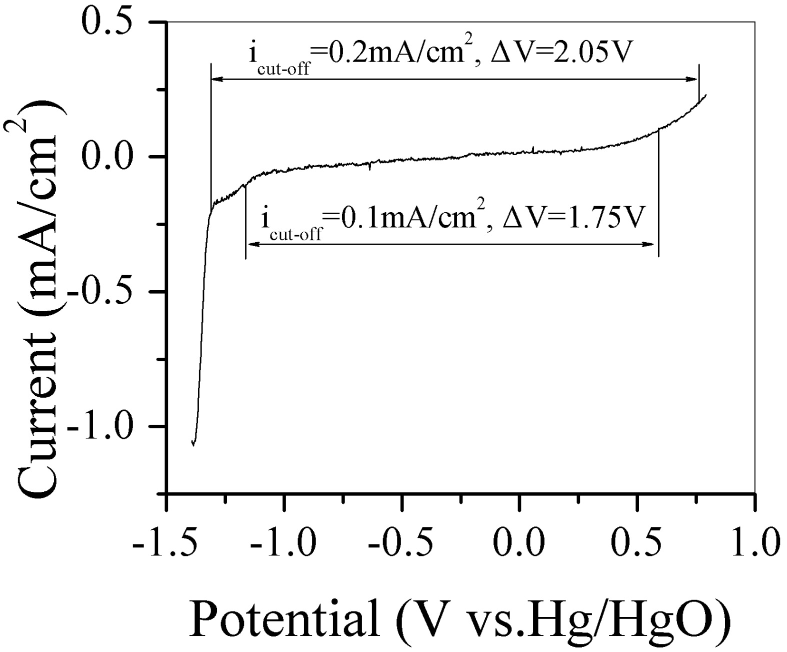


Figure 1. Potentiodynamic experiment curve of graphite electrode in 7 mol·L^{-1} KOH aqueous solution at a scan rate of 10mV·s^{-1}

Generally, current passing the electrode include two parts, Faradaic and non-Faradaic. In order to generate an accurate stability limit, the Faradaic current component corresponding to electrolyte decomposition must be dominant the observed current density. In other words, only when the non-Faradaic, or the capacitive component, on the working electrode can be negligible, the above definition of electrochemical stability will produce a reliable potential window for the electrolyte.

Cyclic voltammetry curves can give some information of capacitive current range. Fig. 2 shows the cyclic voltammetry curve measured on graphite electrode in 7 mol·L^{-1} KOH aqueous solutions at a scan rate of 10 mV·s^{-1}. Clearly, there exists capacitive current density of about 0.1 mA·cm^{-2} and there is an anodic current peak corresponding to oxidation of adsorbed hydrogen at about -1.25V vs. Hg/HgO. Referring to the potential of hydrogen generating, the anodic potential limit on graphite electrode is about -1.25V vs. Hg/HgO (using the anodic current peak of the adsorbed hydrogen), which is consisted with the data of Fig. 1. The oxygen generating will be occurred at the potential of 0.40V vs. Hg/HgO (using the oxidative cyclic voltammetry curve of positive direction, cut-off current density is 0.1 mA·cm^{-2} except capacitive current density) or 0.50V vs. Hg/HgO (using the oxidative cyclic voltammetry curve of positive direction, cut-off current density is 0.2 mA·cm^{-2} except capacitive current density). So the electrochemical stability limits for 7 mol·L^{-1} KOH electrolyte on graphite electrode is about 1.70 or 1.80V when the cut-off current density is 0.1 mA·cm^{-2} and 0.2 mA·cm^{-2}, respectively. From the above data and discussion, it can be concluded that cyclic voltammetry curve gives more information than that of potentiodynamic experiment, the electrochemical stability potential range for 7 mol·L^{-1} KOH electrolyte on graphite electrode from the two methods is about 1.70 or 1.80V.

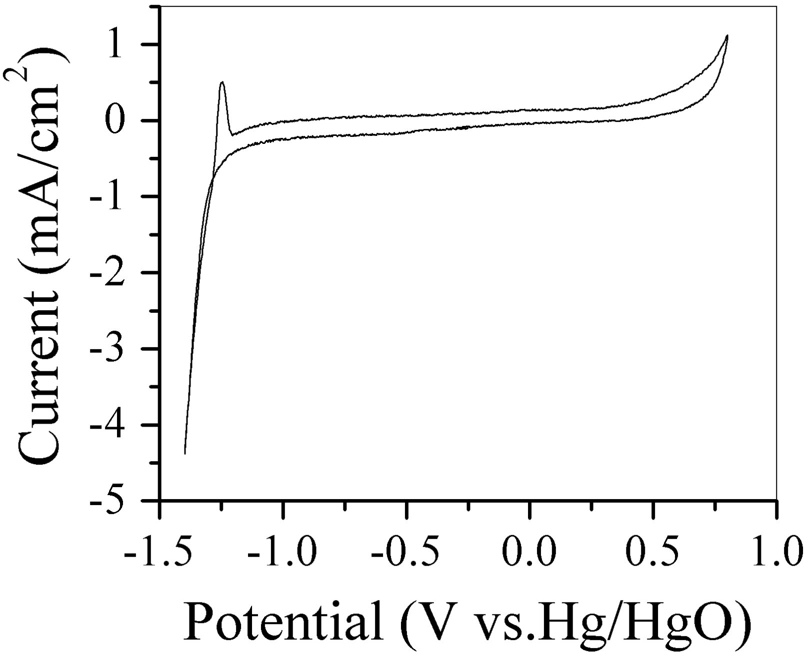
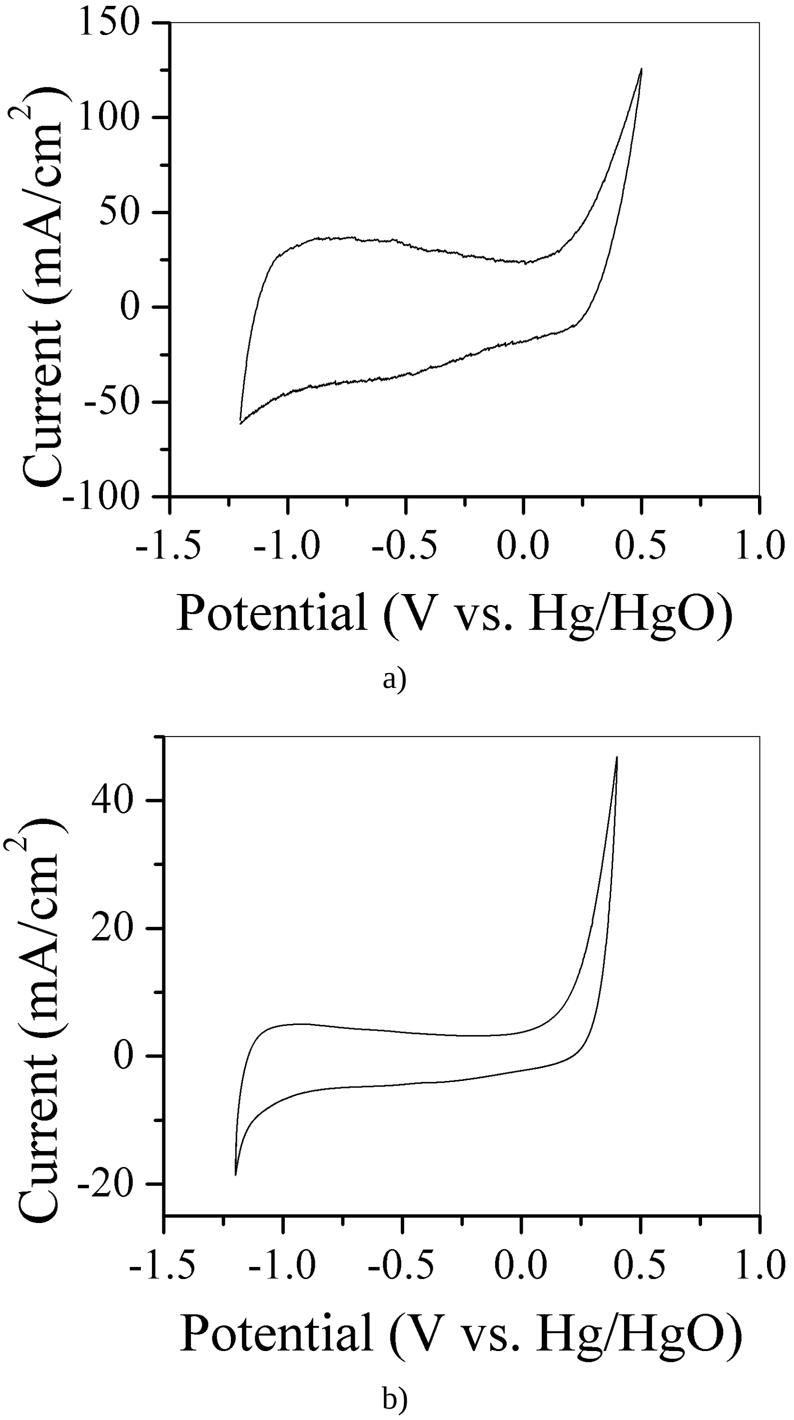


Figure 2. Cyclic voltammetry curve of graphite electrode in 7 mol·L^{-1} KOH aqueous solution at a scan rate of 10mV·s^{-1}

The actual electrodes to which the electrolyte is exposed in real-life electrochemical devices are porous and functional. In electrochemical capacitors, in order to achieve a practically useful capacitance, activated carbon materials with surface area of 10^2-10^3 m^2·g^{-1} should be employed [5]. The resultant capacitive current response in a similar potentiodynamic experiment would then be 5.0 mA·cm^{-2} or larger. Apparently, using 0.1 mA·cm^{-2} or 0.2 mA·cm^{-2} as cut-off current density, the current density is dominated by capacitive current instead of electrolyte decomposition current, and any onset of electrolyte decomposition will be drowned by the overwhelming non-Faradaic noise.

Fig. 3 shows the cyclic voltammetry curve of activated carbon electrode in 7 mol·L^{-1} KOH aqueous solutions. Clearly, at a scan rate of 10 mV·s^{-1} as shown in Fig. 3(a), the average capacitive current density is about 30 mA·cm^{-2}, there is no distinct current peak of hydrogen generating in the anodic territory. It seems that the anodic potential limit on activated carbon electrode is about -1.2V vs. Hg/HgO or lower, because the current corresponding to electrolyte decomposition is confused by the capacitive current. As the scan rate decrease to 1.0 mV·s^{-1} as shown in Fig. 3(b), the average capacitive current density is about 5.0 mA·cm^{-2}, the current peak of hydrogen generating in the anodic territory is visible. The anodic potential limit on activated carbon electrode is about -1.10V to -1.15V vs. Hg/HgO based on the method described in literatures [4]. Similarly, the cathodic potential limit of about 0.15V vs. Hg/HgO at the scan rate of 10 mV·s^{-1} and 0.1V vs. Hg/HgO at the scan rate of 1.0 mV·s^{-1}, respectively, is relatively easy to estimate, because the oxygen generating current is visible upon the capacitive current. Comparing the results of graphite electrode and activated carbon electrode, we know that the electrode with a high specific surface area has a relatively narrow electrochemical stability limits, and the results measured by non-porous inert electrode have little guidance for the electrode with a high specific surface area. The quantification of electrochemical stability limits proposed by Kang Xu, et al [4] can give better information, but a high degree of accuracy need more experiment times and lower scan rate. Furthermore, the assumptions are not always true for the electrodes in electrochemical devices.



a)

b)

Figure 3. Cyclic voltammetry curve of activated carbon electrode in 7 mol·L^{-1} KOH aqueous solution, a) at a scan rate of 10mV·s^{-1} and b) at a scan rate of 1mV·s^{-1}

Generally, new phase, such as gas or solid, will be appeared as electrolyte decomposes. The electrode process will include diffusion of new species. Generally, the impedance of the new diffusion process has a distinct characteristic [8]. To the case of capacitive impedance, the polarization resistance tends to infinity as the frequency tends to zero, e.g., the phase angle tends to be a constant value. Thus, as there a new diffusion process occurs, the phase angle will decrease as the frequency tends to zero. Based on the theory mentioned above, a new method of determining electrochemical stability limits for electrolytes is proposed in the paper.

A series of impedance experiments of activated carbon electrode were carried out, partial curves were shown in Fig. 4. One can see that, at the low frequency band, the phase angle of activated carbon electrode at -1.1V vs. Hg/HgO tends to lower value than that at -1.0V vs. Hg/HgO in the anodic territory. Similarly, the phase angle of activated carbon electrode at 0.1V vs. Hg/HgO tends to lower value than that at 0.0V vs. Hg/HgO in the cathodic territory. This means, the hydrogen generates at about -1.1 V vs. Hg/HgO and the oxygen generates at about 0.1 V vs. Hg/HgO on the activated carbon electrode. Thus the electrochemical stability potential range for 7 mol·L^{-1} KOH electrolyte on activated carbon electrode is about 1.0V. It is obvious that though the impedance method of determining electrochemical stability limits for electrolyte can not give the rate of electrolyte decomposition but can give us a narrower and more accurate electrochemical stability limits. The impedance method of determining electrochemical stability limits for electrolyte is very easy to run, and it needs no complicate data treatment. Using the method described in literatures [4], many experiments of cyclic voltammetry with continuous extended potential limits would be carried out and complicated data treatment must be adopted. Furthermore, if non-faradaic current is not symmetrical, the results based on the literatures [4] will be inaccurate.

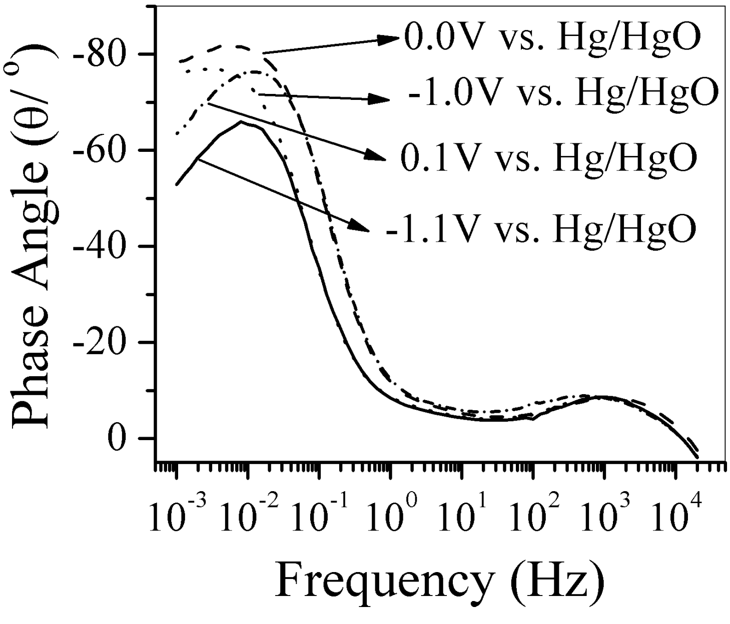


Figure 4. Relationship between phase angle and frequency of impedance of activated carbon electrode in 7 mol·L^{-1} KOH aqueous solutions

Another example is $Ni(OH)_2$/NiOOH electrode. This nano $Ni(OH)_2$/NiOOH electrode with a specific surface area of above 200 $m^2 \cdot g^{-1}$ [7] was used to determine its electrochemical stability limit for 7 $mol \cdot L^{-1}$ KOH electrolyte in the cathodic territory, as shown in Fig. 5. As the electrode potential lower than 0.50V vs. Hg/HgO, the phase angle increases with the frequency decreases at the low frequency range. As the electrode potential reach 0.55V vs. Hg/HgO, the phase angle gets across a maximum and decreases with the frequency decreases at the low frequency range. This is corresponding to the oxygen generation. As the electrode potential reach 0.60V vs. Hg/HgO, the phenomenal of frequency decrease gets more visible. Potential limit on nano $Ni(OH)_2$/NiOOH electrode shows more positive value than that on activated carbon electrode. This mainly attributes to their difference in oxygen generation overpotentials of the two electrodes. On the other hand, it can be see that, the impedance method of determining electrochemical stability limits for electrolyte can be extended over the electrodes with a high surface area and reversible faradaic reactions.

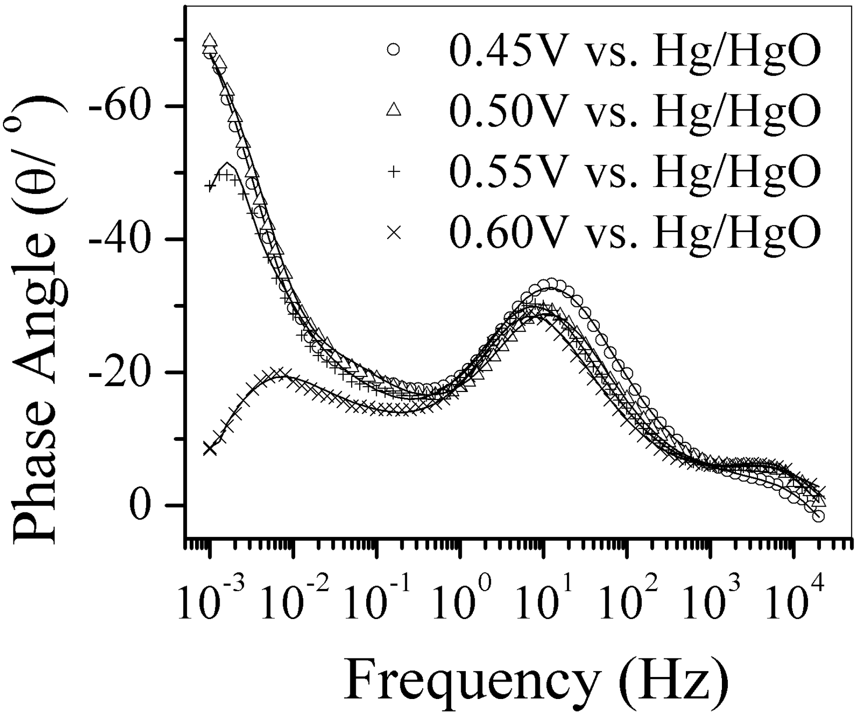


Figure 5. Relationship between phase angle and frequency of impedance of nano- $Ni(OH)_2$/NiOOH electrode in 7 $mol \cdot L^{-1}$ KOH aqueous solution.

Equivalent circuit is commonly used in the analysis of experimental impedance data [8-10], and the behavior of the working electrodes can be described more accurately. But the impedance method mentioned above also has some disadvantages over the conventional approaches, especially when the reactions on the electrodes include underpotential deposition and anodization. As can be seen in the literatures [9] and [10], the impedance plots also show decrease of phase angle at the low frequency range. This is because these desired reactions are also new phase generation processes. Based on the theory of impedance and electrochemical reactions and mechanisms, electrolyte decomposes can be carefully discriminated from others. So, in the condition of combining desired and undesired phase generation processes, the impedance method mentioned above must be extended by combining other techniques for determining electrochemical stability limits for electrolyte.

4. CONCLUSIONS

A new method to accurately determine electrochemical stability for electrolytes is proposed based on impedance study. The method is base the facts that the phase angle of the impedance curve will decrease as the frequency tends to zero when the electrolyte decomposition occurs. This method can accurately determine electrochemical stability for electrolytes on the electrodes of a high surface area. It can be applied to more electrochemical devices than potentiodynamic and cyclic voltammetry. Using the new approach, reliable stability data are obtained for the description of aqueous electrolytes operating in electrochemical capacitors. This new method can also be used to evaluate electrolyte stability in more general systems in which the electrode has a high surface area and reversible faradaic reactions.

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