

# INVESTIGATION ON THE REACTIVITY BETWEEN ORGANIC ACIDS AND GRAPHITE BY A.C. IMPEDANCE SPECTROSCOPY

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## Introduction

Synthesizing graphite intercalation compounds (GICs) with organic acids is a desirable process, because it has the potential to reduce the pollution in the production and the corrosive in use. Electrochemical synthesis of GICs with organic acids has been extensively studied [1,2]. Several organic acids have been successfully selected for synthesizing GICs electrochemically, but there has been limited success and no general guidelines for selecting the acids. Since in electrochemical intercalation, applied electrical potential can always provide sufficient driving force for the oxidation of graphite anode in the Brønsted acid, the essential criteria for the intercalation are puzzling. Despite having a poor oxidizing ability,  $\text{H}_3\text{PO}_4$  and HF, for instance, can still be electrochemically intercalated into graphite under certain condition [3,4]. A review of previous work indicates that only a complex anion, other than a single atom one, can be intercalated in the anodic reactions which relates to the acidity of solution. Furthermore, the formation of mono-valence complex anions which dissolve into polar solvents is required. If these reflect the essence of intercalation, the acidity of organic acids may be the most important influence factor.

A.C. impedance spectroscopy is one of potential tools to analyze electrochemical processes occurring at electrode/electrolyte interfaces, and has been recently applied to analyze the electrochemical intercalation reaction between graphite and intercalates[5]. In this work, we studied the electrochemical intercalation behavior between several acids with different acidity and graphite by

a.c. impedance spectroscopy to obtain the factors that control the electrochemical intercalation.

## Experimental

Natural graphite (NG) with 99.9 wt% carbon content was adopted as the host graphite. NG flakes with diameter of 0.3 mm was compressed to a disk of 1.15 cm in diameter. Reacting graphite materials served as the working electrode. Two platinum plates acted as the counter electrodes.  $\text{Hg}/\text{Hg}_2\text{SO}_4$  electrode served as the reference electrode.

The characteristics of the electrochemical process were investigated by a.c. impedance spectroscopy over a frequency range of 0.01 to  $10^5$  Hz by means of a computerized potentiostat (Solarton SI1287□1255B). To stabilize the reaction system, all electrodes were polarized under a cathodic current density of  $10 \text{ mA cm}^{-2}$  and graphite was immersed into organic acids over night before the measurement. All experiments were performed at ambient temperature. Constant potential of 1.5 V was maintained in each experiment and kept for a sufficient time until the residual current is smaller than  $1 \mu\text{A}$  prior to the experiment. The impedance of the electrode/electrolyte interface was then measured by applying a sine wave of 5 mV rms amplitude over the frequency range of 100 kHz to 0.01 Hz. The measured data were analyzed using a non-linear least-squares fitting program.

## Results and Discussion

Figures 1, 2 and 4 show the a.c. impedance spectroscopy of natural graphite reacting with glyoxylic acid, oxalic acid and formic acid, respectively. In these three cases, there was a semicircle at high scanning frequency and a straight line at low scanning frequency. They proved that these three organic acids could react with natural graphite at the potential of 1.5 V.

Fig.3 shows the a.c. impedance spectroscopy of natural graphite reacting with trichloroacetic acid at different potentials. When the potential is 1.2 V and 1.4 V, the plots close to a straight line. There is no reaction between trichloroacetic acid and natural graphite under this condition. When the potential increases to 1.6 V, the plot is a semicircle. It shows the main electrochemical behavior is the charge transfer at electrode-electrolyte interface. The trichloroacetic acid has been intercalated into graphite layer successfully. Because of the limit of scanning frequency, there is no straight line at low scanning frequency. When the potential is 1.8 V, there are two semicircles in the a.c. impedance spectroscopy. It is a special phenomenon just for trichloroacetic acid. It may come from the stage change of graphite intercalation compounds. The a.c. impedance spectroscopy also shows that natural graphite may react with trifluoroacetic acid at different potential. Its spectroscopy is different from other organic acids.

Table 1 concludes that the reactivity between graphite and the selected organic acids. It shows that the reaction trend between organic acids and graphite become easier with the increase of the acidity of the organic acid. We may understand that the driving force for reaction can be provided by the supplied potential during the electrochemical intercalation. Thus the conductivity of the electrolyte seems more important than the oxidability of the intercalates and the conductivity of the organic acid increases with the acidity of the organic acids.

## Conclusions

A.C. impedance spectroscopy is very useful for the

analysis of the electrochemical process. The formation of the semicircle in the plot proved the occurrence of the reaction. In this study, it could be found that organic acids with low oxidability could be intercalated into graphite layers. With the increase of the acidity of the organic acids, the reaction became much easier.

## Acknowledgement

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## References

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Table 1 Ability of electrochemical formation of GIC in

Organic acid	organic acids	
	pK <sub>1</sub> value <sup>5</sup>	Remarks
Acetic acid	4.76	No reaction
Formic acid	3.75	Intercalation
Glyoxylic acid	3.30	Exfoliation
Oxalic acid	1.27 (pK <sub>2</sub> =4.27)	Anodic reaction observed
Trichloroacetic acid		Self-Exfoliation

\* acidity constant in water at 25□

# in aqueous solution

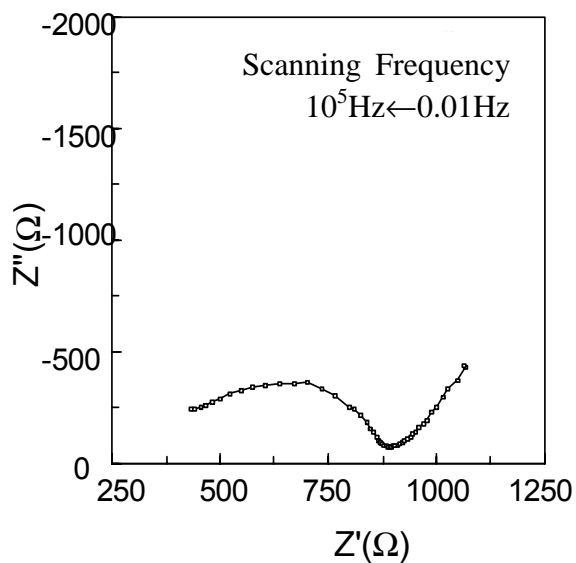


Fig.1 A.c. impedance spectroscopy of natural graphite in glyoxylic acid at 1.5 V

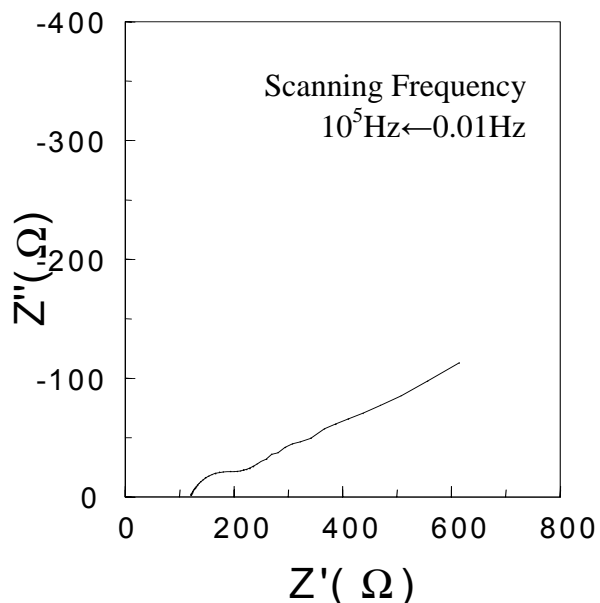


Fig.2 A.c. impedance spectroscopy of natural graphite in oxalic acid at 1.5 V

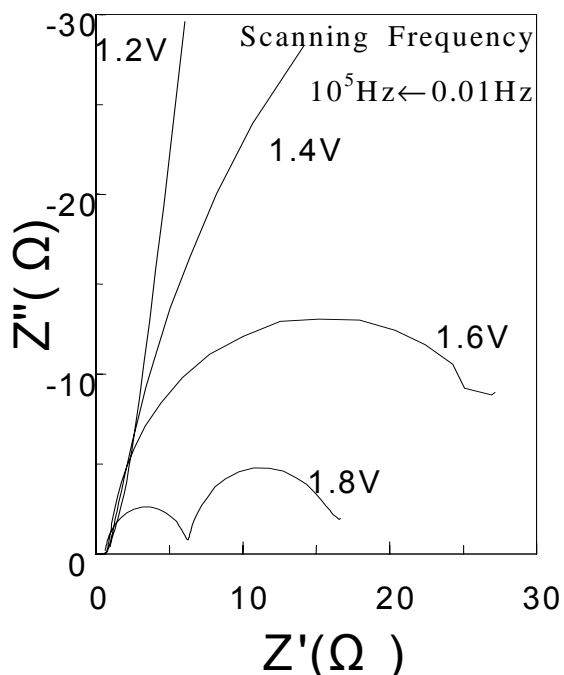


Fig.3 A.c. impedance spectroscopy of natural graphite in trichloroacetic acid at different potentials

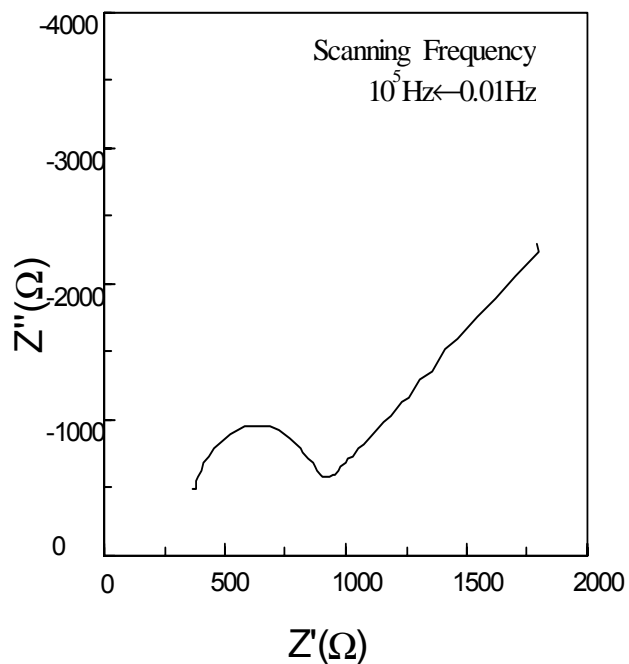


Fig.4 A.c. impedance spectroscopy of natural graphite in formic acid at 1.5 V