

Electrochemical investigation on chlorine and electrolyte intercalation into graphite anodes during magnesium electrolysis process

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Abstract

Cyclic voltammetry (CV) was used to investigate chlorine and electrolyte intercalation into three different graphite anodes from NaCl-KCl-MgCl₂ melts at 700°C. The three anodes were composed of needle-coke (NC), petroleum-coke (FPC) and common petroleum-coke (CPC), respectively. Chlorine intercalation amount was characterized by the reduction current (reduction electricity quantity) on the reverse scan during the cyclic voltammograms. And the electrolyte intercalation was presented by the increase in oxidation charge between the forward scan and the reverse scan during the CV measurements. The results show that among the three graphite anodes, NC shows the lowest reduction current and nearly no increase in the charges, while about 5-10 times increase in the charge for the FPC and CPC. The above results implied that NC has a better resistance to electrolyte and chlorine intercalation, which were confirmed by the electrolysis experiments results. As a simple and useful method, CV can be used to test graphite anode corrosion resistance to electrolyte and chlorine in chloride system.

Introduction

Currently, graphite is the only material of choice to be used as the anode in molten chloride melts, such as in Mg, Li, Na, Ca electrolytic processes. Graphite anodes are slowly consumed and have to be replaced after some time use due to oxidation caused by the cell atmosphere and raw material hydration^[1-5]. In addition, electrolyte and chlorine can intercalate into graphite anode during the electrolysis, which not only results in graphite disintegration and consumption by the reaction with the evolved chlorine, but more importantly in the production of highly toxic C-Cl compounds such as CCl₄, olefins and arenes, etc.^[6-7]. In order to select a long lifetime graphite anode, it is necessary to select kinds of graphite anodes and investigate their corrosion resistance to the chloride melts and chlorine. CV can provide a quick and accurate information on reduction/oxidation currents, which can be used to determine chlorine and electrolyte intercalation currents that is related to the corrosion resistance to the chloride melts and chlorine. In this paper, three graphite materials-NC, FPC, and CPC are selected as the anode and CVs are employed to characterize the chlorine and electrolyte intercalation currents.

Table 1 the tested properties of graphite anodes

Sample property	NC	FPC	CPC
Bulk density(g/cm ³)	1.705	1.575	1.811
Open porosity	14.72%	17.90%	8.17%
Electrical resistivity (μΩ.m)	0.74	0.96	0.85

Graphitization degree	89.07	86.28	89.07
Real density	2.256	2.246	2.256
Ash	500ppm	500ppm	1000ppm

Experimental details

Composition of the electrolyte used in the experiment was composed of NaCl (AR>99.5%), KCl (AR>99.5%), and anhydrous MgCl₂ (AR >99.9%). The NaCl and KCl were dried at 200 °C for 6 h and stored in a glove box for use in the experiments. The anhydrous MgCl₂ was stored in the glove box and used as received. The three graphite materials –needle-coke (NC), fine petroleum-coke (FPC) and common petroleum-coke (CPC) (all made in China) -were used as the working electrodes, respectively. Prior to use, each electrode was fabricated into a 6 mm. diameter rod, and shielded by an alumina tube with an apparent area of 0.45 cm² left exposed. A spectroscopic graphite rod was employed as the reference electrode and a W wire as the counter electrode. And each of the three graphite materials was also manufactured to 10mm ×20 mm ×30mm to serve as an anode for electrolysis, respectively, and a carbon steel was used as cathode. The basic properties of the three graphite materials were measured and listed in Table 1. All the graphite electrodes exposed in the melts were polished thoroughly with 1/0 to 5/0 emery papers, and then degreased by acetone and ethanol before immersion into the melts. Both electrolysis experiments and electrochemical measurements were carried out in an alumina crucible housed in a stainless steel vessel under argon atmosphere at 700°C. Electrochemical measurements were performed using Princeton 2273 potentiostats; data acquisition and processing were carried out by a Powersuite software. All the potentials in the paper were referred to the spectroscopic graphite. After electrolysis graphite anode was taken out from the cell and was observed by SEM after the surface electrolyte was cleaned completely.

Results and discussion

NC material

The typical CVs recorded on NC electrode are shown in Fig.1. A forward scan from 0 to 1.5 V followed by a reverse scan produced Curve 1 of Fig. 1 (a). During the forward scan, there was a small adsorption peak at about 1.0-1.3 V due to chloride ion adsorption on the graphite electrode, it was also observed in the literature^[8]. No distinct reduction current appeared during the reverse scan. But in the second scan (Curve 2 of Fig. 1 (a)), an obvious reduction current can be observed during the reverse scan, indicating that the evolved chlorine was reversibly intercalated into the graphite electrode during the forward scan, and then discharged (or deintercalated) in the reverse scan to give rise to the cathodic current. Such a cathodic current was also observed in a NaCl saturated NaAlCl₄ melts [7]. Moreover, according to

literature [6], Cl_2 evolved in the graphite anode can react with the anode to form some C-Cl compounds. In fact, the maximum deintercalated current for the NC was about 6.3 mA/cm^2 according to the Curve 2 of Fig.1 (a). Cl_2 intercalation into the graphite electrode increases the risk of emitting C-Cl compounds and consuming the graphite anode. The charge consumed during the forward scan from the potential, A, at which chlorine starts to evolve, to 1.6 V is the same as that consumed during the reverse scan from 1.6 V to the potential, B, at which the oxidation current fell to zero, as shown in Curve 2 of Fig. 1 (a). The results indicate that the electrode area did not change, i.e. nearly no electrolyte and chlorine intercalated into the electrode. While during the reverse scan from the potential B to C, the charge decreased by 0.01 C due to the cathodic current generated. When further scan to 2.0 V was performed and then reversed, the Cl_2 intercalation current increased to 48.1 mA/cm^2 (did not give here) and the charge increased by 1.4 C . This is attributed to the increase in working electrode area caused by chloride electrolyte intercalation under Cl_2 -assistance, similar to the chloroaluminate melts system in which the chlorine intercalation compound has already been determined [7]. The consumed charge increased by 3.0 C due to more electrolyte intercalation into the graphite anode under Cl_2 -assistance when first scanned from the potential A to 4.0 V followed by a reverse scan to the potential B, as shown in Fig.1 (b).

Petroleum-coke (PC) materials

The FPC was similar to the NC in that there was no distinct reduction current for the first scan from 0 to 1.5 V . But for the second scan from 0 to 1.6 V followed by a reverse scan (Fig 2 (a)), the Cl_2 deintercalation current density reached 62.5 mA/cm^2 , far more than that for the NC, which implies more chlorine intercalated into the FPC. The chlorine oxidation current quantity increased by 2.15 C (from about 0.2 C to 2.35 C) when scan from the potential, A, of the onset Cl_2 evolution to 1.6 V then reversely scan to the potential, B, where the oxidation current fell to zero, as shown in Fig. 2(a), indicating that the working area increased by more than ten times as much as the original one. While the chlorine evolution current quantity increased by 4 C during the reverse scan from 4.0 V (Fig. 2(b)).

The CPC showed a large reduction current even during the first reverse scan from 1.5 to 0 V , reaching a current density of 56.8 mA/cm^2 , indicating a high reactive activity of the graphite material to Cl_2 evolution (Fig.2(c)). During the second scan from 0 to 1.6 V and then back to 0 V , the chlorine intercalation current reached 62.5 mA/cm^2 , and the increase in chlorine evolution current quantity of 3.3 C was the largest among the three graphite anodes, which was caused by the biggest increase in the working electrode area – about 165% . In the anodic scan from the potential, A, where chlorine starts to evolve, to 4 V and back to the potential, B, where anodic current fell to zero, the chlorine evolution current quantity increased by 5 C in Figure 2(b), the largest value among the three electrodes. These results demonstrate that the CPC anode is the worst at preventing electrolyte and chlorine intercalation. By comparison of the chlorine evolution potentials shown in the CVs, CPC graphite electrode exhibited a lower chlorine evolution potential than NC and FPC. This may be caused by the fact that it contains more impurities than FPC, and these impurities may act as catalysts for chlorine evolution and for chlorine and electrolyte intercalation. The reaction between the chlorine and the graphite electrode may lead to a depolarization effect on chlorine evolution, so giving a lower chlorine evolution potential than FPC.

Electrolysis results

After 6 h electrolysis at the current density of 1 A/cm^2 at $700 \text{ }^\circ\text{C}$ under argon atmosphere, the NC, FPC and CPC anodes exhibited a different change in the surface morphology, as shown in Figure 3. Obviously, the NC graphite anode is characterized by a less change in the surface after electrolysis compared with the original

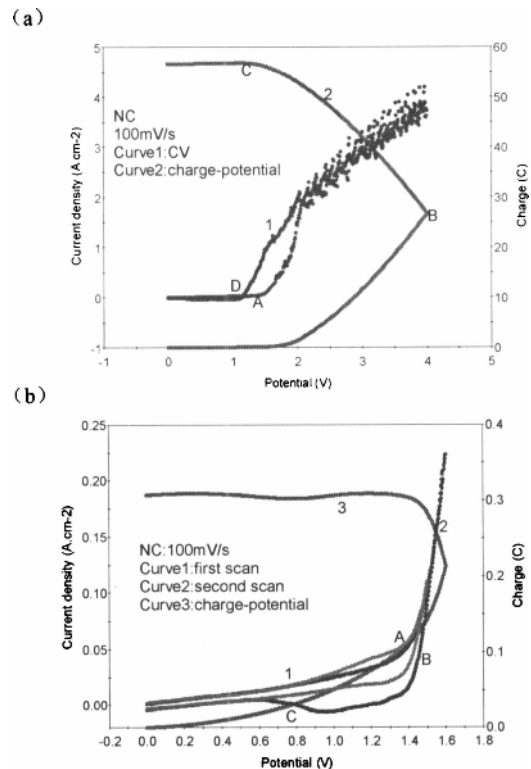


Fig.1 Cyclic voltammograms for NC in NaCl-KCl-MgCl_2 melt at $700 \text{ }^\circ\text{C}$. WE: $\text{C}(0.45 \text{ cm}^2)$, RE: spectroscopic graphite, CE: W wire .

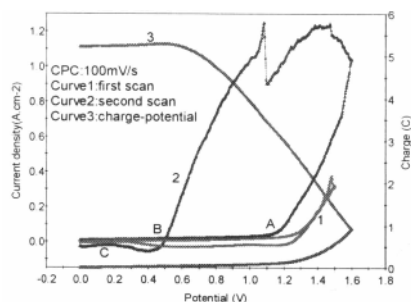
morphology before electrolysis, especially no distinctly new cracks occur under the SEM observation scale in Fig.3(a). While at the same electrolysis conditions, both CPC and FPC graphite anodes exhibited a distinct consumption in the surface and the occurrence of new cracks in the surface in Figure 3 (b) and 3 (c), especially for FPC graphite anodes, long and deep crack was observed, this may related to the relatively worse properties, such as a lower graphitization degree shown in Table 1. Moreover, electrolyte intercalation into CPC graphite anode is remarkable. The higher impurity content of CPC graphite may be the main reason caused by the electrolyte intercalation. The crack appearance in the FPC and CPC is related to chlorine and electrolyte intercalation, but the specific relation remains still unknown. The above results indicate that the NC graphite behaves a better corrosion-resistance to the chloride melts at high temperature than FPC and CPC, in good accordance with the CV analysis. Therefore, CV analysis is a simple and efficient method to compare the graphite anode behaviors in chloride melts and further to be used in selection of a suitable anode in chloride melts.

Conclusions

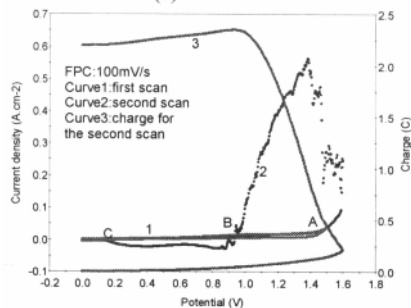
CV analysis has determined that the NC anode generated a far smaller chlorine intercalation current, as well as a lower electrolyte intercalation amount than the two PC electrodes, but presented a higher chlorine evolution potential. The CPC exhibited a larger electrolyte intercalation amount, and a lower chlorine evolution potential than that of FPC electrode.

Acknowledgements

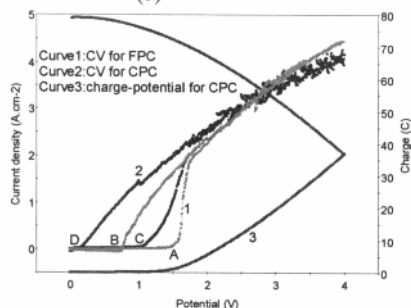
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(a)



(b)



(c)

Fig.2 Cyclic voltammograms recorded on (a) FPC and (b) FPC and CPC (c) CPC in NaCl-KCl-MgCl₂ melt at 700 °C. WE: FPC(0.45cm²), CPC(0.45cm²); RE: spectroscopic graphite; CE: W wire .

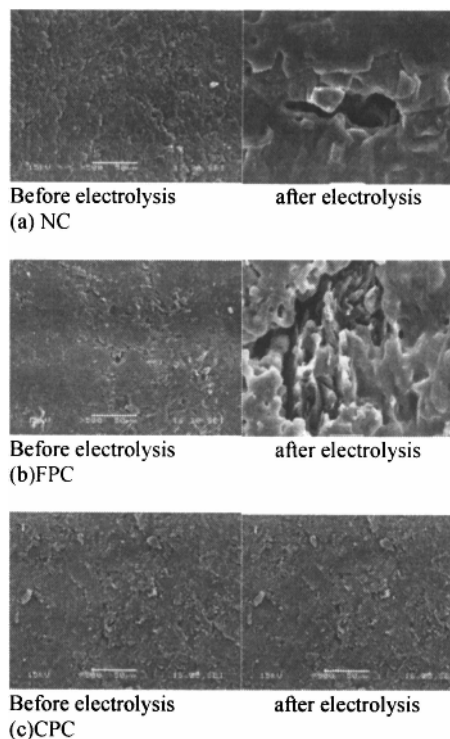


Figure 3 The SEM morphology of NC, FPC and CPC before and after 6h electrolysis at 700 °C

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