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煤及其含氧基团模拟物的电化学还原

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摘要: 以四丁基溴化铵作支持电解质电化学还原煤及其含氧基团模拟物,用甲醇萃取电化学还原前后的煤. 还原产物和萃取物由气相色谱-质谱联用仪定性分析,煤含氧基团模拟物的电还原产物用气相色谱定量分析. 结果表明,经电化学还原后,煤表面含氧基团减少,需进一步提高煤含氧基团模拟物的转化率. 电化学测试同时给出还原过程中各相关电极反应的动力学方程.

关键词: 煤; 煤含氧基团模拟物; 电化学还原

中图分类号: O646

文献标识码: A

煤是我国主要的一次能源. 煤中约有85%动力煤直接用于燃烧,造成严重的大气污染. 大气污染有90%的SO₂是燃煤产生的,1995年我国全年SO₂总排放量达到27.3Mt. 形成的酸雨污染区,曾达到国土总面积的40%(1997年已降为约30%),这对人民生活以及工业生产造成的严重污染,已引起国内外的广泛关注^[1]. 也因此,洁净煤技术^[2]在中国刻不容缓,特别是煤中硫分的脱硫.

煤脱硫的方法主要有物理脱硫法、化学脱硫法、生物脱硫法、电化学脱硫法等,其中煤的电化学脱硫凭借其独特的优点一直备受关注. 电化学脱硫法又可细分为电化学氧化脱硫和电化学还原脱硫. 研究发现,电化学还原脱硫若与浮选相结合即可大大提高脱硫效果^[3].

煤浮选脱硫之电化学还原法实际包含黄铁矿和细粒煤两方面的研究内容. 关于黄铁矿的电化学还原,国内外学者已有较深入的研究^[4-7]. 但是,有关细粒煤在电化学还原后发生的具体变化和导致细粒煤可浮性增加的原因仍需要进一步探索.

煤中影响浮选的含氧基团主要有羧基、羰基、羟基和醚键等. 含氧基团越多,亲水性越强,越不利于分选. 利用电还原反应还原煤中芳环侧链的含氧基团,便可增强煤的疏水性,有利于煤炭分选的进行.

本文研究了煤及其含氧基团模拟物的电化学还原,为电化学还原浮选脱硫提供理论参考依据.

1 实验条件和方法

1.1 实验药品

苯甲酸、苯甲醛、苯乙酮、四丁基溴化铵、乙醚、甲醇、平朔煤(该煤样工业分析见表1).

表1 平朔煤样的工业分析

Tab. 1 The proximate analysis of pingshuo coals

Coal sample	Proximate analysis		
	M _{ad} % (by mass)	A _{ad} % (by mass)	V _{daf} % (by mass)
Pingshuo coals	1.65	28.57	31.20

M_{ad}: moisture, A_{ad}: ash, V_{daf}: volatile matter

1.2 实验仪器

IM6e 电化学工作站(德国 Zahner 公司)、Agilent6890 型气相色谱(美国 Agilent 公司)、HP6980/5973 型气相/质谱联用仪(美国惠普公司)、电解槽(自制:以铂为阳极、铅为阴极)、YJ-44 型稳压电源、JB-3 型定时恒温磁力搅拌器、HANGPING FA2104 型电子天平、DZF-3 型真空干燥箱.

1.3 实验方法

室温下,以四丁基溴化铵作为支持电解质电化学还原煤及其含氧基团模拟物,用甲醇萃取电化学还原前后的煤. 由气相色谱-质谱联用仪(GC/MS)分析电化学还原前后煤的甲醇萃取物及其含氧基团模拟物的电还原产物;另外用气相色谱(GC)定量分析煤含氧基团模拟物的电还原产物. 相关电化学测试使用 IM6e 电化学工作站.

2 结果与讨论

2.1 电化学还原产物的 GC/MS 分析

图 1 分别示出煤含氧基团模拟物苯甲酸、苯甲醛和苯乙酮电还原产物的总离子流色谱. 经解析后发现:苯甲酸和苯甲醛电还原后均含 3 个主要组分,即为苯甲酸、苯甲醛和苯甲醇;而苯乙酮电还原后主要含苯乙酮和 2,6-二甲基-1-苯酚两个组分.

由此推测,对应的还原过程当为苯甲酸先被还原为苯甲醛,苯甲醛再进一步被还原为苯甲醇;但苯甲醛也可能在电还原过程中部分地被氧化成苯甲酸;2,6-二甲基-1-苯酚是苯乙醇的同分异构体,可认为是苯乙酮电还原后的产物.

表 2 表明,原煤甲醇萃取物含氧基团的物质品种比较多,相对含量也不低,这些都是浮选脱硫的不利因素. 但如表 3 所给,原煤经电化学还原后,其甲醇萃取物中的含氧基团物质的品种已有所减少,且整体含量降低. 由此可见,应用电化学方法还原煤的含氧基团是可行的,而且效果较好.

图 2 分别是原煤甲醇萃取物(a)和原煤电化学还原产物甲醇萃取物(b)总离子流色谱,比较之下,两者相差甚大. 参照表 2、表 3,原煤经过电化学还原后其物质组分确实发生了反应. 表现在含氧基团物质品种和含量相对减少,疏水性增强.

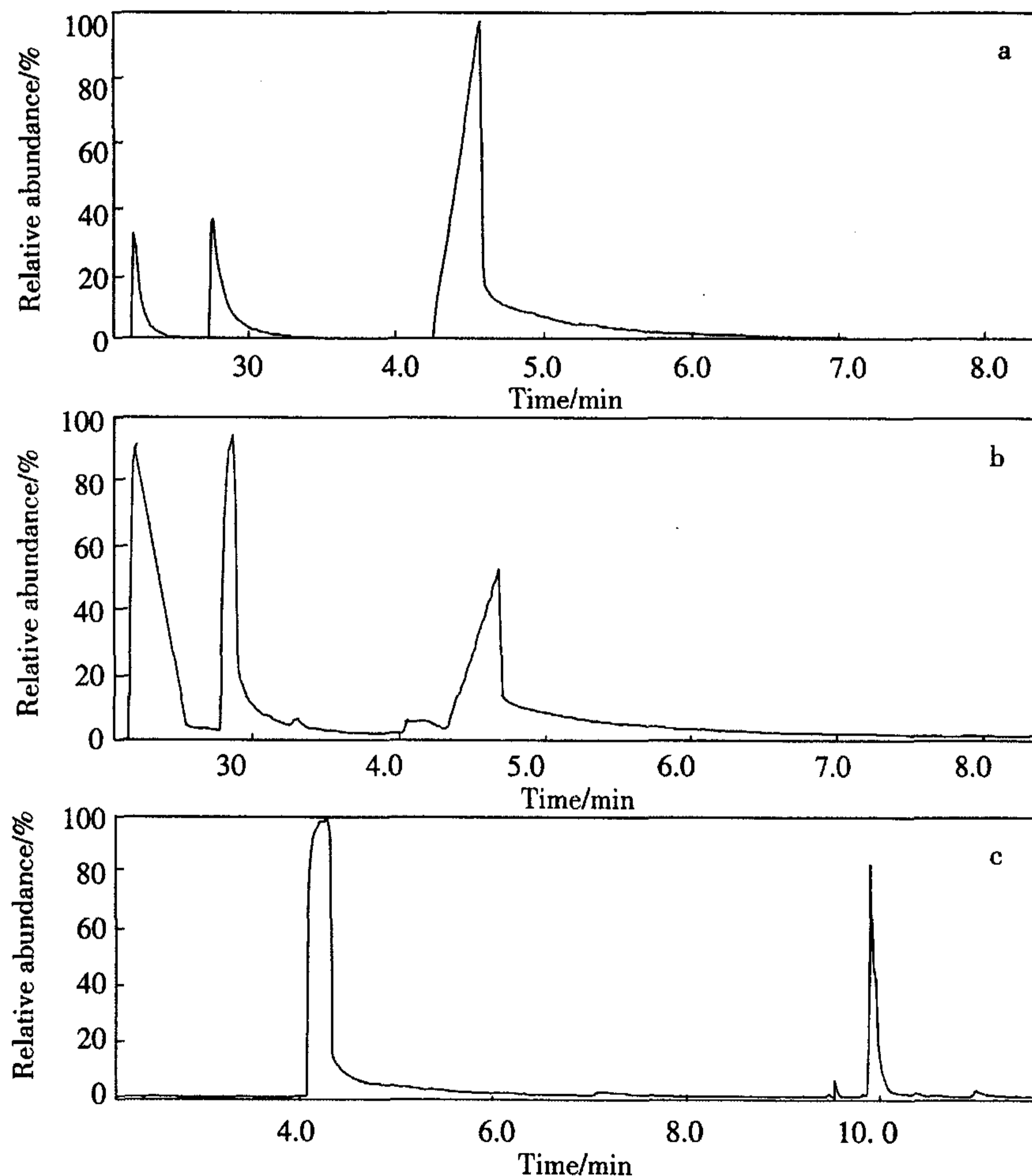


图 1 煤含氧基团模拟物的总离子流色谱 a) 苯甲酸, b) 苯甲醛, c) 苯乙酮

Fig. 1 Total ion chromatogram of the oxygenic functional simulacrum of coals

a) benzoic acid, b) benzaldehyde, c) acetophenone

表2 原煤甲醇萃取物组分

Tab.2 Extractive compositions of the original coals extracted by methanol

Peak No.	Compound	Molecular formula	Molecular weight	Relative content/%
1	1-naphthol	C ₁₀ H ₈ O	144.06	9.049
2	heptadecane	C ₁₇ H ₃₆	240.28	1.516
3	methyl palmitate	C ₁₇ H ₃₄ O ₂	270.26	1.580
4	icosane	C ₂₀ H ₄₂	282.33	0.469
5	16-methyl-methyl heptadecanoate	C ₁₉ H ₃₈ O ₂	298.29	1.094
6	4,4'-(1-methylidene) bisphenol	C ₁₅ H ₁₆ O ₂	228.12	1.782
7	2,2'-methylenebis[6-(1,1'-dimethylethyl)-4-methyl] phenol	C ₂₃ H ₃₂ O ₂	340.24	2.413
8	methyl behenate	C ₂₃ H ₄₆ O ₂	354.35	0.495
9	methyl tetracosanoate	C ₂₅ H ₅₀ O ₂	382.38	1.718

表3 原煤电化学还原产物甲醇萃取物组分

Tab.3 Extractive compositions of the deoxidized products of coals extracted by methanol

Peak No.	Compound	Molecular formula	Molecular weight	Relative content/%
1	tributyl amine	C ₁₂ H ₂₇ N	185.21	8.671
2	pentadecane	C ₁₅ H ₃₂	212.27	1.486
3	hexadecane	C ₁₆ H ₃₄	226.27	0.390
4	octadecane	C ₁₈ H ₃₈	254.30	0.613
5	enndecane	C ₁₉ H ₄₀	268.31	1.354
6	icosane	C ₂₀ H ₄₂	282.33	0.618
7	methyl palmitate	C ₁₇ H ₃₄ O ₂	270.26	1.544
8	heneicosane	C ₂₁ H ₄₄	296.33	0.941
9	methyl stearate	C ₁₉ H ₃₈ O ₂	298.29	1.654
10	methyl behenate	C ₂₃ H ₄₆ O ₂	354.35	2.031
11	methyl tetracosanoate	C ₂₅ H ₅₀ O ₂	382.38	2.136

2.2 气相色谱分析

采用外标法^[8]测定煤含氧基团模拟物电还原转化率,结果如下:

苯甲酸还原生成苯甲醛的转化率为5.2%;

苯甲酸还原生成苯甲醇的转化率为11.7%;

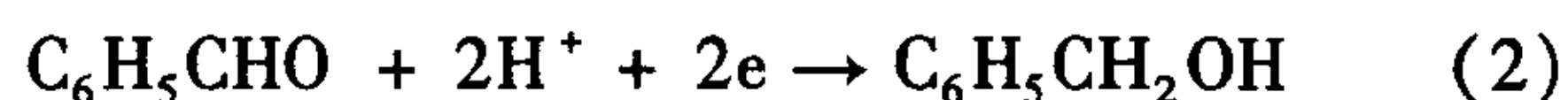
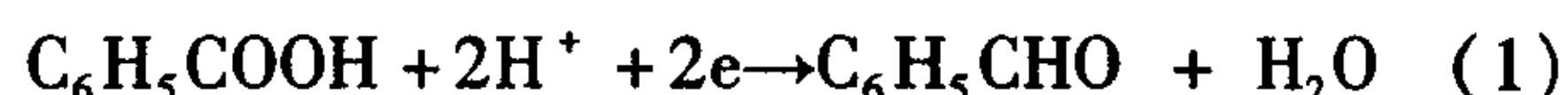
苯甲醛还原为苯甲醇的转化率为2.7%;

苯乙酮还原为2,6-二甲基-1-苯酚的转化率为2.7%.

2.3 循环伏安测试

图3分别示出苯甲酸(a)、苯甲醛(b)、苯乙酮(c)以及原煤(d)电化学还原的循环伏安曲线,扫描电位区间+4.0~-4.0 V.扫速100 mV/s.

由图3 a可见, $I \sim E$ 曲线于-1.41 V和-3.45 V附近各出现一还原峰,对应的峰电流为-6.91 mA和-7.00 mA.据苯甲酸电还原产物质谱分析推知,上述电极反应当为:



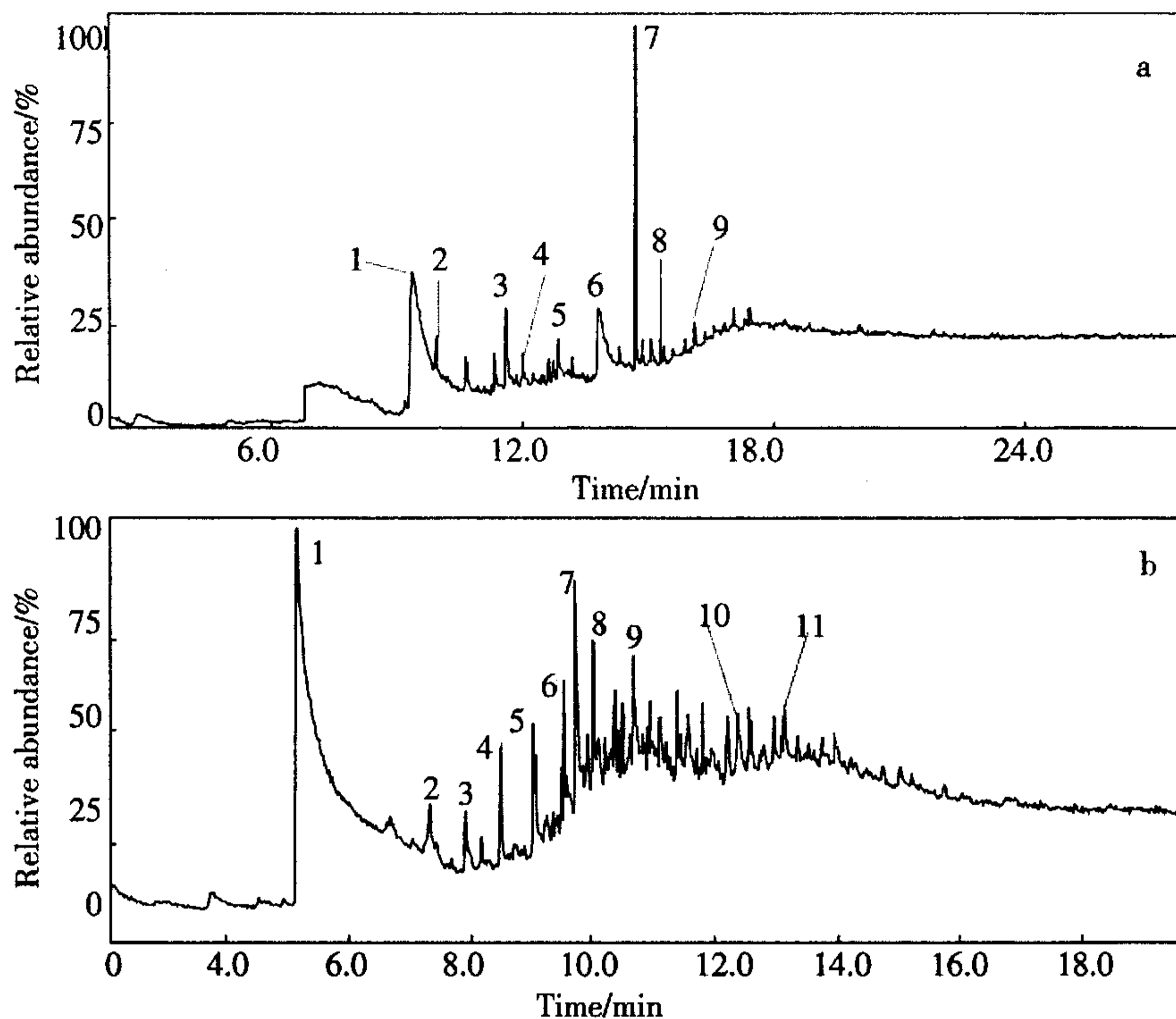


图2 原煤(a)及其电化学还原后(b)的甲醇萃取物总离子流色谱
 Fig.2 Total ion chromatogram of extractive compositions for the original coals(a) and deoxidized coals(b) extracted by methanol

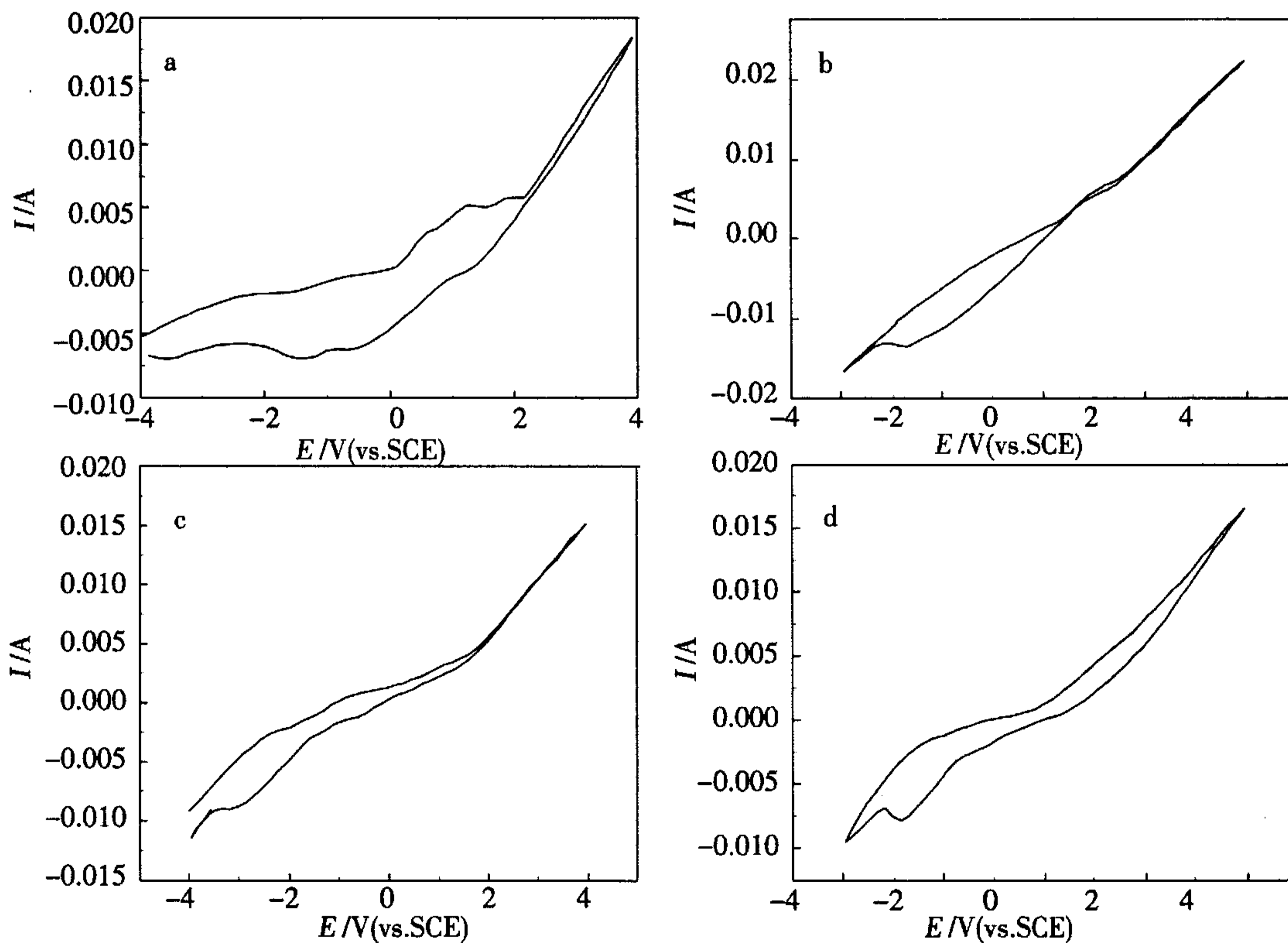


图3 原煤及其含氧基团模拟物的循环伏安曲线
 Fig.3 Cyclic voltammograms of the original coals and its oxygenic functional simulacrum
 a) benzoic acid, b) benzaldehyde, c) acetophenone, d) coals
 scan rate: 100 mV/s

又从图3 b可知,苯甲醛于-2.76 V处显示一还原峰,峰电流-13.66 mA. 参照苯甲醛电还原产物质谱分析,推知与该峰对应的电极反应为:



关于苯乙酮,其于-3.15V产生一阴极还原峰,峰电流-8.88mA(见图3 c). 从苯乙酮电还原产物质谱分析推知与该还原峰对应的电极反应为:

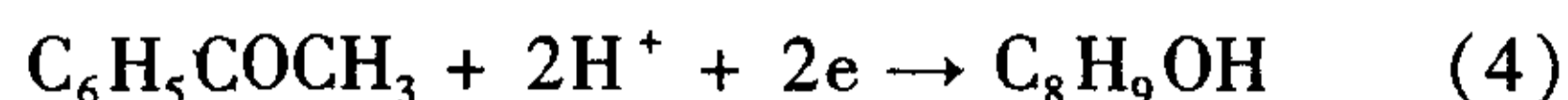


图3 d中原煤于-2.87V处出现一阴极还原峰,峰电流-7.87mA. 从表2可推知,煤含氧基团化合物的稳定性各不相同,因此电还原反应的难易也不同.

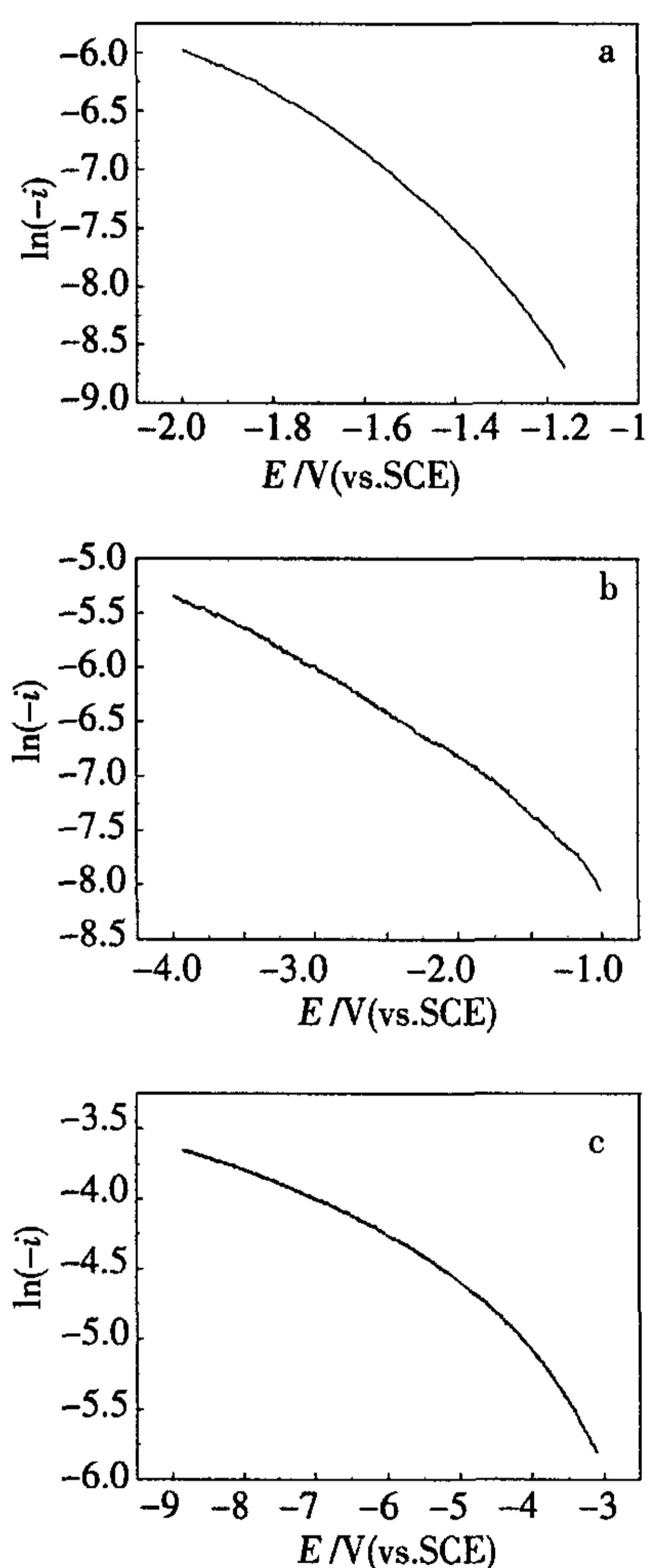


图4 煤含氧基团模拟物的稳态极化曲线

Fig. 4 Polarization curves of the oxygenic functional simulacrums of coals

a) benzoic acid, b) benzaldehyde, c) acetophenone scan mode: dynamic scan, scan rate: 5mV/s

2.4 稳态极化曲线的测定

图4给出苯甲酸(a)、苯甲醛(b)和苯乙酮(c)的稳态极化曲线.

图4 a中, $\ln(-i) \sim E$ 基本成线性关系, 回归方程 $\ln(-i) = -12.00096 - 3.12881E$. 这就是苯甲酸电还原反应式(1)的速率方程. 图4 b的 $\ln(-i) \sim E$ 也基本成线性关系, 回归方程 $\ln(-i) = -8.62188 - 0.85945E$. 此即苯甲醛电还原反应式(3)的速率方程. 从图4 c即可看出, 其 $\ln(-i) \sim E$ 的线性关系稍差些, 近似的线性回归方程为 $\ln(-i) = -7.23854 - 0.52291E$. 大体上可认为这一回归方程仍可代表苯乙酮电还原反应式(4)的速率方程.

3 结论

1) 煤经电化学还原后, 其表面含氧基团的品种和整体含量都有所减少.

2) 煤含氧基团模拟物经电化学还原后, 表面含氧官能团减少, 疏水性增强.

以上表明: 应用电化学方法还原煤以降低其表面含氧基团是可行的.

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Electrochemical Reduction of Coals and the Oxygenic Functional Simulacrums of Coals

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Abstract: Electrochemical reduction of coals and the oxygenic functional simulacrums of coals has been studied. In this process, tetrabutylammonium was used as supporting electrolyte. The coal and the deoxidized coal were extracted by methanol. Qualitative analysis of the deoxidized products and the extractives was carried out on gas chromatograph-mass spectrometer. The deoxidized products of the oxygenic functional simulacrums of coals were analysed quantitatively with gas chromatograph spectrometer. The results show that the oxygenic functional groups on the coals surface decrease and the translation ratios of the oxygenic functional simulacrums of coals need further increase after electrochemical reduction,. The electrochemical tests show simultaneously the kinetics equations of every related electrode reactions during the reduction.

Key words: coals; the oxygenic functional simulacrums of coals; electrochemical reduction