化学学报 1994 52 (1): 23-28 ISSN: 0567-7351 CN: 31-1320/06

OH-存在下四苯基卟啉合钴氧化过程的电化学和光谱电化学

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收稿日期 修回日期 网络版发布日期 接受日期

摘要 本文利用薄层伏安和现场光谱电化学方法考察了在EtCl~2中OH^-存在下四苯基卟啉合钴(TPP)Co^11的电极氧化反应。在低浓度OH^-存在下, (TPP)Co^11与OH^-生成一配位的配合物(TPP)Co^11(OH)^-, 此配合物不可逆地被氧化为(TPP)Co^111(OH)^-, 氧化峰电位负移到0.53V。而卟啉环第一步氧化电位也负移到0.88V。在高浓度OH^-存在下, (TPP)Co^11(OH)^-氧化生成(TPP)Ca^111(OH)~2^2-,氧化电位随OH^-浓度增加向负移。卟啉环第一步和第二步氧化电位分别负移到0.57V和1.07V。同时观察到第二步氧化伴随后行化学反应, 产物氧化电位在1.32V。测定了(TPP)Co^11(OH)^-, (TPP)Co^111(OH)^-和(TPP)Co^111(OH)~2^2-,(TPP)^+Co^111(OH)^-和(TPP)^+Co^111(OH)~2^2-各级配位化合物稳定常数。提出一个在OH^-滴定过程中(TPP)Co的各步配位反应及电化学反应的机理。

关键词 反应机理 钴络合物 电化学反应 卟啉 络合反应 电极反应 氢氧根

分类号 0646

Electrochemistry, spectroelectrochemistry of (TPP)Co in the presence of OH- anions

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Abstract In the presence of OH- anions, electrochem. redox reactions of cobalt tetraphenylporphyrin ((TPP)Co) were investigated in dichloroethane solution by thin-layer cyclic voltammetry and spectroelectrochem. In the presence of OH-, OH- was axially coordinated to (TPP)CoII to generate (TPP)CoII(OH)-. This complex was oxidized to (TPP)CoIII(OH) at Eo' = 0.53 V (vs. SCE). The Eo' for the first porphyrin-ring oxidation was neg. shifted to 0.88 V. When the amount of added OH- anions was more than two equivalent amount, no second OH- coordination reaction was found. Electrochem. oxidation reaction of (TPP)CoII(OH)- generated (TPP)CoIII(OH)21- species. The half-wave potential of this reaction was shifted neg. with increasing OH- concentration The first and second porphyrin-ring oxidns. occurred at Eo' of 0.57 V and 1.07 V, resp. A chem. reaction following the second oxidation step was observed and a reversible redox step of the reaction product was observed at 1.32 V. Mechanism for the coordination and electrochem. reactions of (TPP)Co in the OH- titration process are proposed. Stability constants for various complexes are calculated

Key words REACTION MECHANISM COBALT COMPLEX ELECTROCHEMICAL REACTION PORPHYRIN COMPLEX REACTION ELECTRODE REACTION HYDROXIDE RADICAL

DOI:

通讯作者