

论文

聚乙烯亚胺-钴络合物对氧还原电流的影响

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收稿日期 2003-10-27 修回日期 2003-12-7 网络版发布日期 接受日期

摘要 研究了聚乙烯亚胺-钴络合物 (PEI-Co) 在电解质溶液中的氧可逆结合特性及对氧还原电流的影响. PEI-Co 络合物溶解于电解质的水溶液中, 在氧气气氛中络合物与氧结合, UV-Vis 光谱在 310nm 处出现了新的吸收峰, 并在 280nm 处观察到等吸光点. PEI-Co 络合物与氧结合平衡曲线服从 Langmuir 行为, 络合物与氧结合的亲和力 (p_{50}) 为 0.667kPa. 氧与 PEI-Co 加成物的解离反应表观速率常数为 $1.1 \times 10^5 \text{ s}^{-1}$, 表明络合物具有快速、可逆的氧结合特性. 在 PEI-Co 络合物存在下, 氧电极的还原电流显著增加, 并且随 PEI-Co 络合物的浓度以及气氛中氧浓度的增加而增加. $[\text{PEI 链节}]/[\text{Co}]=5/1$ 时, 氧还原电流达到极大值, 说明 PEI-Co 络合物与氧形成了结构为 $[\text{N}_5\text{Co}^{\text{III}}-\text{O}_2-\text{Co}^{\text{III}}\text{N}_5]$ 的加成物.

关键词 [聚乙烯亚胺钴络合物](#) [氧可逆结合](#) [氧电极](#) [还原电流](#)

分类号

EFFECT OF THE POLYETHYLENEIMINE-COBALT COMPLEX ON REDUCTION CURRENT OF OXYGEN

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Abstract The reversible oxygen-binding properties of the polyethyleneimine-cobalt (PEI-Co) complex and the effect of the PEI-Co complex on the reduction current of oxygen were studied. The color of the PEI-Co complex in the electrolyte solution changed on exposure to oxygen atmosphere, which was monitored by UV-visible absorption spectrometry. The UV-visible absorption spectra of the PEI-Co complex displayed a new adsorption band at 310 nm, with an isosbestic point at 280 nm. The spectral change was attributed to the reversible oxygen-adduct formation of the PEI-Co complex even in the electrolyte solution. The oxygen-binding equilibrium curve of the PEI-Co complex obeyed a Langmuir isotherm, to give the high oxygen-binding affinity ($p_{50}=0.667 \text{ kPa}$). And the apparent dissociation rate constant of oxygen from the PEI-Co complex ($k_d=1.1 \times 10^5 \text{ s}^{-1}$) was also high. The aqueous solution of the PEI-Co complex that had rapid and reversible oxygen-binding properties functioned as an oxygen-enriching medium for oxygen electrode to enhance the diffusion-controlled current for the oxygen reduction. Based on the rapid release of oxygen from the PEI-Co complex, a high current was obtained for the reduction of oxygen in the presence of the PEI-Co complex, and the current increased with the increase of the concentration of the PEI-Co complex and the oxygen concentration in the atmosphere. The reduction current reached a saturated value near $[\text{ethyleneimine unit}]/[\text{Co}]=5$, which suggested the structure of a six-coordinate μ -dioxo dinuclear complex $[\text{N}_5\text{Co}^{\text{III}}-\text{O}_2-\text{Co}^{\text{III}}\text{N}_5]$. A new type of oxygen-diffusion electrode for metal / air batteries and fuel cells is proposed using the oxygen-enriching material immobilized at the electrode surface.

Key words [Polyethyleneimine-cobalt complex](#) [Reversible oxygen-binding](#) [Oxygen electrode](#) [Reduction current](#)

DOI:

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