



Separation of platinum and ruthenium by a sulphoxide modified polystyrene resin in laboratory column systems



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ABSTRACT

The present study deals with the adsorption performance of fixed bed columns using powdered sulphoxide modified poly(styrene-co-divinylbenzene) ($d_{10} < 13 \mu\text{m}$, $d_{50} < 30 \mu\text{m}$, $d_{90} < 50 \mu\text{m}$) for the separation of platinum and ruthenium from hydrochloric acidic solutions containing both metals ($c_{\text{Pt}} = 20 \text{ mg/L}$, $c_{\text{Ru}} = 10 \text{ mg/L}$). The influence of hydrochloric acid concentration, temperature, flow rate, flow direction, redox potential and bed height on the breakthrough characteristics was examined. Platinum was separately adsorbed mainly induced by hydrochloric acid concentration and redox potential keeping platinum as Pt^{IV} and ruthenium as Ru^{III} . Ruthenium was separately adsorbed to 90% essentially induced by hydrochloric acid concentration, temperature and redox potential keeping platinum as Pt^{IV} and ruthenium predominantly as Ru^{IV} . Experimental data at optimised separation conditions were fitted to different kinetic models (Thomas, Yoon–Nelson, Bohart–Adams, Wolborska) to characterise the fixed bed column behaviour. Adsorption of both metals was well described by Thomas and Yoon–Nelson model with correlation coefficients $R^2 \geq 0.95$ whereas Bohart–Adams and Wolborska model were less suitable.

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1. Introduction

Handling the world energy supply is always an actual topic and becomes more and more key issue for the future of humankind. Long-term scarcity of crude oil, gas and coal associated with global environment pollution requires exploitation of renewable energy sources. The further demand of mobile devices with battery longevity leads to the development of new portable low power systems because current rechargeable batteries have reached their theoretical energy density limits. For that purpose fuel cells exhibit high efficiency and high potential for environment-friendly energy conversion leading to a significant reduction of fossil fuel use. Proton exchange membrane fuel cells (PEMFC) as well as direct liquid fuel cells (e.g. direct methanol fuel cell (DMFC), direct ethanol fuel cell (DEFC)) are prime candidates for mobile application due to their compactness and portability. According to the theoretical energy density of pressurized hydrogen (3000 Wh/L) and methanol–water mixtures (3400 Wh/L), fuel cell systems can make more energy available than Li-ion batteries ($\sim 1300 \text{ Wh/L}$) achieving longer operating periods at the same volume [1]. A big drawback is the elemental necessity of significant amounts of costly platinum group metals (PGMs) as catalysts at which carbon supported

platinum and platinum–ruthenium mixtures (1:1 atomic ratio) have emerged as best among all other catalysts [2]. Both metals are rare and mining is expensive hampering the broad commercialisation of fuel cell technology. The growing demand makes development of efficient and environmentally friendly recycling processes necessary. Catalyst recycling of exhausted fuel cells lowers manufacturing costs, reduces mining of primary sources and accordingly protects the environment. The classical route is a pyrometallurgical process. After stack dismantling, the membrane electrode assembly (MEA) is separated, shredded and incinerated followed by manifold extraction, solution and precipitation steps. Unfortunately incineration holds the adverse effect of releasing aggressive and toxic hydrofluoric acid what necessitates special linings as well as laborious gas scrubber. The hydrometallurgical route offers an alternative at which both metals are leached using strong oxidising acidic solutions [3]. Ruthenium is separated via distillation as its volatile tetroxide and platinum via precipitation or solvent extraction [4]. These processes are well established but offer disadvantages. Special design and construction materials are needed for distillation because volatile ruthenium compounds are highly explosive and extremely poisonous. Precipitation of platinum may be cheap but demands large quantities of precipitating agent and generates a lot of waste. Solvent extraction requires costly amounts of toxic and/or flammable organic solvents and consumes a lot of time due to multiple extraction steps. One useful

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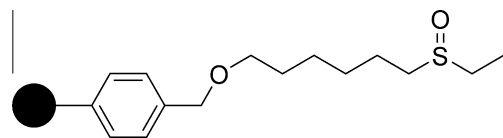


Fig. 1. Structure of sulphoxide modified poly(styrene-co-divinylbenzene) resin (1).

solution for the separation of platinum and ruthenium from hydrochloric acidic solutions is adsorption. Fixed bed adsorption is an efficient and effective method conducting sorption processes for industrial applications when a suitable low cost adsorbent is available. In any case, design of adsorption column needs numerous parameters to be adapted.

This study deals with the solid-phase extraction (SPE) of platinum and ruthenium from artificial hydrochloric acidic solutions using powdered sulphoxide modified poly(styrene-co-divinylbenzene) ($d_{10} < 13 \mu\text{m}$, $d_{50} < 30 \mu\text{m}$, $d_{90} < 50 \mu\text{m}$) as adsorbent (Fig. 1). Catalyst separation refers to the complex of problems which actually exist for PEMFC and DMFC recycling. This lab-scale research provides fundamental findings for prospective large-scale recovery of fuel cell catalyst similar to the contemporary industrial recycling of automobile catalyst converters. The replacement of oil addicted combustion engines by fuel cells will be inevitable due to the shortage of fossil resources.

Hydrochloric acid concentration (c_{HCl}), temperature (T), flow direction, flow rate (Q), redox potential (E_0) and bed height (h) were sequentially varied and adapted to achieve separately adsorption. The experimental data at optimised conditions were fitted to Thomas, Yoon–Nelson, Bohart–Adams, Wolborska model to characterise the fixed bed column behaviour.

2. Experimental

2.1. Materials

The synthesis of powdered sulphoxide modified poly(styrene-co-divinylbenzene) resin **1** (1% cross-linked, sulphoxide loading: 2.2 mmol/g, $d_{10} < 13 \mu\text{m}$, $d_{50} < 30 \mu\text{m}$, $d_{90} < 50 \mu\text{m}$) as adsorbent was already described by us [5]. Hydrochloric acid ($c_{\text{HCl}} = 9.5 \text{ mol/L}$, suprapur) was obtained from Merck KGaA and used as received. Water was purified by a Milli-Q Reference ultrapure water purification system. This high purity water was used for preparation of all stock solutions and dilutions. The platinum starting material was yellow solid $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.99%) from Alfa Aesar. The ruthenium starting material was black crystalline $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (99.99%) from Alfa Aesar. Sodium hydroxide was used as 0.1 M NaOH Titrisol solution supplied by Merck. Anhydrous stannous(II) chloride was obtained as white crystalline SnCl_2 (for synthesis) from Merck.

2.2. Instruments

Fixed bed column studies were performed with SPE cartridges (Agilent technologies) 5.5 cm in height (H) and 0.5 cm in internal diameter (d). For higher temperatures a special glass coated column (self-construction) 5.5 cm in height and 0.5 cm in diameter was used. Fractions were collected by PrepFCTM fraction collector (Gilson). Different temperatures were established using a MLW thermostat U2 (VEB MLW). Different flow rates were adjusted using peristaltic pump Minipuls 3 (Gilson). Redox potential was determined using a Sentix ORP single-rod measuring cell (Pt–Ag–AgCl) containing 3 M KCl electrolyte (WTW). Infrared spectra were recorded using FTIR-Nexus (Thermo Nicolet) fitted with a Smart Orbit sample system (Diamond) for resins (transmission mode with 32 scans and a resolution of 8 cm^{-1}).

2.3. Preparation of stock solution

Stock solution of Pt^{IV} ($c_{\text{Pt}} = 400 \text{ mg/L}$) was made by dissolving the appropriate amount of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 9.5 M HCl (suprapur).

The composition of commercial hydrated ruthenium trichloride ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) is diffuse and hydrochloric acidic solutions contain by the majority Ru^{IV} as miscellaneous monomeric as well as chloride- and oxygen-bridged polymeric complexes (e.g. $[\text{Ru}(\text{OH})_n\text{Cl}_{6-n}]^{2-}$, $[\text{Ru}_2\text{O}(\text{H}_2\text{O})_n\text{Cl}_{10-n}]^{n-4}$, $[\text{Ru}_2\text{O}_2(\text{H}_2\text{O})_n\text{Cl}_{8-n}]^{n-4}$ etc.) just as nitrosyl species (e.g. $[\text{RuNOCl}_5]^{2-}$) [6]. A solution of commercial $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ($c_{\text{Ru}} = 200 \text{ mg/L}$) dissolved in hot 9.5 M HCl became deeply brown. UV/Vis spectrum revealed characteristic absorption for dimeric complexes $[\text{Ru}_2\text{O}_2\text{Cl}_4(\text{H}_2\text{O})_4]$ and $[\text{Ru}_2\text{OCl}_{10}]^{4-}$.

Unified stock solution of Ru^{III} ($c_{\text{Ru}} = 200 \text{ mg/L}$) was made of commercial $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ dissolved in ethanol and refluxed under argon atmosphere until the brownish solution became green [7]. Ethanol was removed under reduced pressure and the residue dissolved in 9.5 M HCl (suprapur) becoming a green solution. Argon was passed into solution to remove oxygen and preventing oxidation. Storage overnight at room temperature turned the colour to strawberry red. UV/Vis-spectrum matched with spectrum of $[\text{RuCl}_6]^{3-}$ [8] and showed no further Ru^{IV} absorption.

Stock solution of Ru^{IV} ($c_{\text{Ru}} = 200 \text{ mg/L}$) was made by passing chlorine through a hot Ru^{III} stock solution which became deeply brown ($E_0 = 1.10 \text{ V}$, $T = 25 \text{ }^\circ\text{C}$, $c_{\text{HCl}} = 9.5 \text{ mol/L}$). UV/Vis-spectrum matched with spectrum of $[\text{RuCl}_6]^{2-}$ [8]. Acidity of stock solutions was standardised by titration using 0.1 M NaOH solution as titrand and phenolphthalein as indicator (intrinsic colour of ruthenium disappeared due to dilution before end-point was reached). Solutions of lower acidity and metal concentration ($c_{\text{Pt}} = 20 \text{ mg/L}$, $c_{\text{Ru}} = 10 \text{ mg/L}$) were obtained by appropriate dilution with deionised water as required at which equal volumes of appropriate dilutions were united.

Sn^{II} stock solutions ($c_{\text{Sn}} = 65 \text{ mg/L}$) for stannometric titrations were made freshly every time and promptly used due to oxidation by atmospheric oxygen. The appropriate amount of anhydrous SnCl_2 was dissolved in a small volume of boiling 9.5 M HCl (suprapur) until a clear solution was obtained. Acidity was adjusted by filling-up with deionised water and 9.5 M HCl (suprapur) as needed.

All stock solutions were standardised by ICP–OES and stored on a dark cold place.

2.4. Methods

2.4.1. Adsorption

Experimental conditions in detail are listed in Table 1.

Metal content of the feed solution referred to realistic leaching results. An exhausted MEA ($A = 25 \text{ cm}^2$, anode: $m_{\text{Pt}} = 2 \text{ mg/cm}^2$, $m_{\text{Ru}} = 1 \text{ mg/cm}^2$, cathode: $m_{\text{Pt}} = 1 \text{ mg/cm}^2$, Nafion[®] membrane) from a direct methanol fuel cell was treated with chlorine saturated concentrated hydrochloric acid ($V = 100 \text{ mL}$) at reflux for four

Table 1

Experimental conditions of various adsorption experiments for adsorption of platinum and ruthenium onto resin **1**.

parameter	experimental conditions
Hydrochloric acid (mol/L)	0.1, 1.0, 3.0, 6.0, 9.5
Temperature ($^\circ\text{C}$)	25, 60, 90
Flow rate (mL/min)	0.1, 0.5, 1.0
Bed height (cm)	0.4 ($m = 50 \text{ mg}$), 0.8 ($m = 100 \text{ mg}$)
c_{Pt} (mg/L)	20
c_{Ru} (mg/L)	10
Column height (cm)	5.5
Internal column diameter (cm)	0.5

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