

PORPHYRIN BASED-SYSTEMS FOR THE DETECTION OF RECOVERABLE METALS FROM LI-ION BATTERIES. MINI-REVIEW

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ABSTRACT

The collection and recycling of metals, especially heavy metals, from all types of batteries is a major requirement of European Countries. Market studies highlighted that in the rechargeable battery field, lithium batteries are environmental friendly alternatives to the more polluting Ni–Cd batteries. Although lithium is not expected to bioaccumulate and its human and environmental toxicity are low, one source of lithium with impact to the environment is spent lithium batteries, due to the large variety of Li salts incorporated in polymer electrolyte membranes. Concerning to cathode, new trends are based on nanostructured lithium iron and manganese phosphate. Whatever are the metals involved in the cathode of batteries (Co-Ni-Mn-Fe) the problem of controlling the efficiency of metals recovery is implying the use of sensor devices. In this paper we are concerned on porphyrin –based sensor devices for the rapid and accurate detection of Li, Ni, Mn.

INTRODUCTION

Because Li based batteries are considered electric energy storage systems characterized by high energy/power density, which is the most important demand of electric vehicles [1] attention is also focused to diminish the negative environmental effects of batteries and waste batteries [2]. In spite of their low content in metals many efforts are concentrating to collect and recycle [3] of all types of batteries.

Li- AND OTHER METAL- SALTS INCORPORATED INTO POLYMERIC MEMBRANES AND IN THE CATODE OF THE BATTERIES.

Due to their applications in lithium rechargeable battery technology, a large variety of Li salts [4] are studied for being incorporated in polymer electrolytes, such as: LiSbF₆, LiF, LiCl, LiBr, LiI, lithium perchlorate (LiClO₄), lithium arsenate (LiAsF₆), lithium tetrafluoroborate (LiBF₄), lithium triflate (LiCF₃SO₃), and lithium bis(trifluoromethane sulfone)imide (LiN(SO₂CF₃)₂), lithium bis-perfluoroethylsulfonyl imide LiN(SO₂C₂F₅)₂. Although the environmental toxicity Li is low, one of the main sources of lithium having impact to the environment is spent lithium batteries [5].

New formulations of cathode are based on nanostructured lithium iron or manganese phosphate. Whatever are the metals involved in the cathode of batteries (Co-Ni-Mn-Fe) the technology to recover different metals will stay feasible as the non ferrous metallurgy for those products is always based on Sulphuric Acid. The sensor devices are more often used for controlling the efficiency of metals recovery. In this paper we are concerned on porphyrin –based sensor devices for the rapid and accurate detection of Li, Ni, Mn due to the fact that porphyrins are forming 1:1 complexes with almost all metals [6].

PORPHYRIN BASED-SYSTEMS FOR THE DETECTION OF RECOVERABLE METALS FROM LI-ION BATTERIES

Li DETECTION. Lithium is the most important element for lithium battery, but also in clinical treatment of depression. Thus, a new goal is finding of inexpensive methods for the determination of lithium and its separation and collection by recycling. Octabromoporphyrin, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin, (H_2P^{4-}), (**Figure 1, structure a**), a water-soluble porphyrin, was demonstrated to react with lithium ion in aqueous alkaline solution to form LiP^{5-} , of which formation constant was $10^{-18.81 \pm 0.02}$ mol dm^{-3} for $K_{LiP} = [LiP^{5-}][H^+]^2[Li^+]^{-1}[H_2P^{4-}]^{-1}$. Reactions were 10^3 - 10^4 times faster comparatively to more planar unbrominated porphyrin derivatives [7]. This kind of structure is highly electron deficient, producing a decrease of the basicity of porphyrin due to the presence of eight bromine atoms that are attach in the β -pyrrole positions [8]. A spectrophotometric method for the determination of lithium in aqueous solution was also reported, by using the same porphyrin [9]. The calibration graph was linear over the range of 0.007–0.7 mg cm^{-3} (1×10^{-6} – 1×10^{-4} mol dm^{-3}) of lithium (I) with a correlation factor of 0.967. By this method the determination of lithium as low as 10^{-5} M in the presence of Na^+ greater than 0.1 M could be done. The selectivity of $Li^+ : Na^+$ is higher than 10^4 [10].

Mn DETECTION. The determination of manganese in environmental samples is a need because acute exposure to manganese generates chemical pneumonitis and chronic exposure may lead to dementia [11]. The oxidation states of manganese are ranging from -3 to $+7$, but the most abundant species is Mn^{2+} , followed by Mn^{3+} and Mn^{4+} . Anodic stripping voltammetry analysis of trace amount of Mn(II) was reported and it is based on chemically modified bentonite–*meso*-tetra laural porphyrin (**Figure 1, structure b**) carbon paste electrode. In this method Mn(II) gives well-defined voltammetric peak in the pH range of 3.5–7.5. The detection limit is 1.07×10^{-7} mol L^{-1} Mn(II). The peak currents increase linearly with Mn(II) concentration over the range of 6.0×10^{-7} to 5.0×10^{-4} mol L^{-1} . The selectivity is very high, so that an excess of 1000-fold of the additive ions had not interferences on the determination of Mn(II).

Co DETECTION. PVC-based membranes having as ionophore 5,10,15,20-tetraphenylporphyrin together with sodium tetraphenylborate as an anion excluder have been investigated as potentiometric sensors for Co(II) [12]. Calibration graphs were linear from 0.008–100 mM-Co(II) and the response time was 20 s. The membrane was stable for 4 months and showed good selectivity for Co(II) over other cations, although Na(I) and Ni(II) interfered at high concentrations.

Ni DETECTION. Due to the fact that the nickel toxicity generates various diseases such as: pneumonitis, dermatitis and asthma, its accurate determination is important. In this respect, more nickel-selective potentiometric electrodes [13, 14] based on two symmetrical different porphyrins as ionophores: *meso*-tetraphenylporphyrin and *meso*-tetra-*p*-tolylporphyrin (**Table 1, structures c and d**) were realized, by varying the nature of solvent mediators and the ratio of of the membrane components. Both of the electrodes exhibit preference to nickel ions, but the silver ion interferes in both of the cases; for the *meso*-tetra-*p*-tolylporphyrin based electrode, the lead ions interfere too [14]. It may be concluded that the electrodes have a moderate selectivity. The nickel-selective electrode based on *meso*-tetraphenylporphyrin as ionophore presents a better potentiometric response comparatively to the *meso*-tetra-*p*-tolylporphyrin based one, when using the next composition for the membranes: 1 wt.% ionophore, 66 wt.% *o*-nitrophenyloctylether (*o*-NPOE), 33 wt.% PVC (plasticizer : PVC = 2 : 1) and sodium tetraphenylborate 20%mol. relative to the ionophore. The response was linear in the range (5×10^{-4} – 1×10^{-1} M). By using another solvent mediator, dibutylphthalate, the best result was given when using the membrane incorporating *meso*-tetra-*p*-tolylporphyrin, sodium tetraphenylborate and solvent mediator in PVC in the ratio (7 : 35 : 4 : 54), exhibiting

Nernstian response in the concentration range 5.6×10^{-6} – 1.0×10^{-1} mol/l between pH 2.5–7.4 and a fast response time of 20 s [13].

A new membrane, having in composition *meso*-tetrakis-{4-[*tris*-(4-allyl dimethylsilyl)-phenyl]-silyl}-phenyl}porphyrin (**Figure 1, structure e**) [15]; sodium tetraphenyl borate: PVC in the ratio 5:5:150, exhibited Nernstian response in the activity range 2.5×10^{-6} to 1.0×10^{-1} M, over wide pH range (2–5.5) with a fast response time (8 s). The sensor can be used in partially non-aqueous media up to 20% (v/v) content of methanol or ethanol and acetone and over a period of 4 months.

New trends in finding of suitable analytical methods for metal detection are focused on incorporation of dyes into hybrid materials, such as silica glasses. The main advantages of this solution is that glasses prepared from the sol–gel process are transparent, making them suitable for spectrophotometric analysis, are chemically, photochemically and thermally stable making them proper for use in harsh environments [16]. A novel metal ion sensor for Zn^{2+} and Ni^{2+} was prepared using silica monolith doped with *meso*-tetra(*p*-carboxyphenyl) porphyrin (**Figure 1, structure f**). The doped material was prepared using TEOS:EtOH:H₂O:HCl:porphyrin molar ratios of $1:5:7:3.1 \times 10^{-2}:2.3 \times 10^{-5}$, respectively. The metal coordinated to the silica monolith could be removed by washing with 1 M HNO₃ [17].

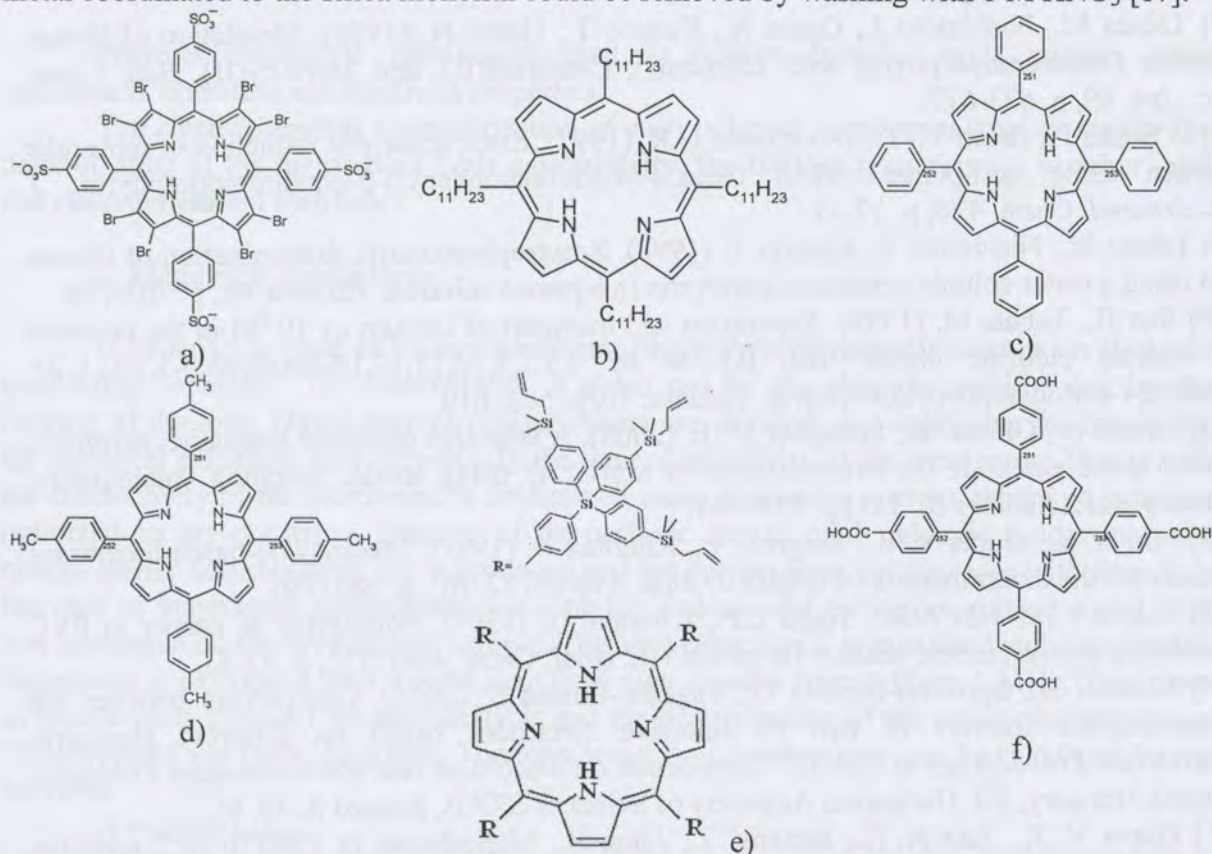


Figure 1. The structures of ionophores: 2,3,7,8,12,13,17,18 -octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (a); *meso*-tetra laural porphyrin (b); *meso*-tetraphenylporphyrin (c); *meso*-tetra-*p*-tolylporphyrin; *meso*-tetrakis-{4-[*tris*-(4-allyl dimethylsilyl)-phenyl]-silyl}-phenyl}porphyrin (e); *meso*-tetra(*p*-carboxyphenyl) porphyrin (f).

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