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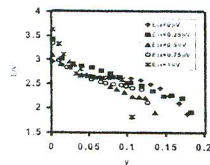
EFFECT OF Cr FOR Mn SUBSTITUTION ON THE Li<sup>+</sup> ION INSERTION IN NICKEL MANGANITES WITH SPINEL STRUCTURE.

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Among the materials used as cathodes for Li<sup>+</sup> ion insertion, those that are frequently used include transition metal oxides with three-dimensional structures as spinel and hollandite [1,2]. One of the most studied is the spinel LiMn<sub>2</sub>O<sub>4</sub>, a material that is easy to prepare, is inexpensive and has low toxicity. However, the Li<sup>+</sup> ion insertion electrochemical capacity ( $y = \text{mol Li}^+$  ion inserted / mol oxide) and, therefore the battery performance, decays in a relative short time [3]. It has been found that  $y$  is associated with a high average manganese oxidation state ( $Z > 3.5$ ). When  $y$  is high, a cationic redistribution in the spinel lattice is produced which provokes a decrease in  $Z$  values. For this reason many current investigations are dedicated to obtaining derivatives of the LiMn<sub>2</sub>O<sub>4</sub> spinel via substitution of small amounts of manganese by other metals with the goal to maintain a high  $Z$ . This work studies the effect on  $y$  induced by the substitution of manganese by chrome, in spinels with the general formula NiCr<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> (with  $x = 0; 0.25; 0.5; 0.75; 1$ ).

The oxides were prepared by the thermal decomposition of the corresponding nitrates. The spinel phase was obtained at 800 °C and was characterized by X-ray diffraction. The cationic distributions that were proposed present a good agreement with the theoretical and experimental cell parameter values. The electrochemical performance was studied in Swagelok cells where the cathode was the oxide, the anode was pure lithium, and the electrolyte was LiBF<sub>4</sub> dissolved in EC-DMC [1]. The discharged curves were obtained at 30  $\mu\text{A}/\text{cm}^2$  and ambient temperature between the OCV and 2 V (Fig. 1). The greater Li<sup>+</sup> ion insertion was found for the oxide NiCr<sub>0.25</sub>Mn<sub>1.75</sub>O<sub>4</sub> ( $y = 0.19$ ). The lithium insertion increases with  $x$  only until  $x=0.25$ . A good correlation was also found between  $y$  and the Mn<sup>3+</sup>/Mn<sup>4+</sup> ratio.

Fig. 1. Li<sup>+</sup> ion insertion in NiCr<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> electrode

## PRODUÇÃO TÉCNICO CIENTÍFICA DO IPEN DEVOLVER NO BALCÃO DE EMPRÉSTIMO

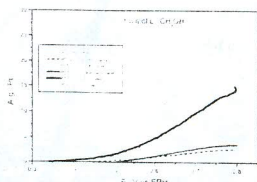
### A COMPATIVE STUDY ON PtRu/C ELECTROCATALYSTS PRODUCING METHODS FOR METHANOL ELECTRO-OXIDATION IN PEM FUEL CELL

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The need for more efficient energy conversion is presently evident as the world fossil fuel sources become scarcer and the cost of the fuels rises. Moreover, the urgent necessity of reducing the pollution in large urban centers imposes the use of non-polluting fuels, like hydrogen and renewable primary fuels in large scale. Fuel cells have shown to be an interesting and very promising alternative to solve the problem of clean electric power generation with high efficiency.

In this work electrocatalysts containing platinum-ruthenium nanoparticles dispersed on high surface area carbon were prepared by different methods: formic acid, citric acid, Bonnemant, IPEN IPT and using a bimetallic precursor (Pt-Ru complex). The comparative study includes a commercial E-TEK electrocatalyst. The Pt-Ru/C (atomic ratio 1:1, 20 wt%) electrocatalysts have been studied for methanol oxidation (Fig. 1) using the thin porous rotating technique.

Figure 1: Anodic scans in a 1.0 mol/L methanol solution with electrocatalysts prepared by different methods,  $v = 10 \text{ mV/s}$ 

The potential region around 0.6 and 0.7 V is of great interest for the operational regime of fuel cells operating with direct oxidation of methanol. In this region can be observed that the electrocatalyst obtained from Pt-Ru E-TEK present the best values of current intensity per gram of platinum. However, the complex method showed to be very promising for practical application in PEM fuel cells.

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## Electrochemical Investigation multidoped Lithium manganate as positive electrode material for Li- Batteries.

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## Abstract:

The spinel compound  $\text{LiCu}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.25}\text{O}_4$  is prepared by a Sol-Gel method using citric acid, ethanol and ammonia solutions. The electrochemical properties are characterized in the voltage range of 2.5-5.5 V vs. Li/Li<sup>+</sup>. X-ray diffraction patterns of a:  $\text{LiMn}_2\text{O}_4$  and b:  $\text{LiCo}_{0.25}\text{Cu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.25}\text{O}_4$  samples showed good crystallinity. The pattern of  $\text{LiMn}_2\text{O}_4$  sample has the distinct peaks at  $2\theta$  of 18.70°, 37.7°, 44° and 48° corresponding to the 111, 311, 222, 400 and 331 diffraction lines, respectively as reported in the literature. On the other hand,  $\text{LiCo}_{0.25}\text{Cu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.25}\text{O}_4$  shows the following characteristic peaks: 30.86°, 36.38°, 44.24° and 58.56°.

Cyclic voltammetric results of the previous compound showed some reversible plateaus at 3.09, 4.05, 4.62, 4.95 and 5.05V on oxidation. These plateaus are attributed to the insertion of Li<sup>+</sup> ion to the spinel structure, oxidation of Mn<sup>3+</sup> to Mn<sup>4+</sup> ( $\text{LiMn}_2\text{O}_4 \rightarrow \text{LiMnO}_2$ ), oxidation of Ni<sup>2+</sup> to Ni<sup>3+</sup>, oxidation of Cu<sup>2+</sup> to Cu<sup>3+</sup> and oxidation of Co<sup>3+</sup> to Co<sup>4+</sup>, respectively. The prepared multi-doped lithium manganate material delivers a high initial capacity of about 155vs.143mAh/g for  $\text{LiMn}_2\text{O}_4$ . This cathode material was also studied by SEM and XRD.

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## EFFECT OF PHYSICO-CHEMICAL PROPERTIES OF APROTIC DIPOLAR SOLVENTS ON THE Li-S BATTERIES PERFORMANCE

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Li-S batteries are very attractive as high-energy rechargeable batteries because of the high theoretical specific energy of the Li/S couple – about 2600 Wh/kg. But despite their attraction Li-S batteries are not used in practice because of essential decreasing of sulfur electrode capacity during its cycling.

The reason for this phenomenon is still not fully understood. As the electrochemical reduction of sulfur involves liquid-phase chemical and electrochemical reactions and is accompanied by formation of poorly soluble compounds, it is necessary to expect, that the depth and efficiency of a sulfur electrode cycling will be rather sensitive both positive electrode composition and physicochemical properties of electrolyte systems. Therefore we in detail investigated the electrochemical behavior of sulfur electrode in electrolyte systems with various compositions. Sulfolane, 3-methoxythiolane, propylene carbonate were as the base solvents, and ethers of a various nature (tetrahydrofuran, dioxolane, glyme, diglyme and tetraglyme) were co-solvents.

It is established that the electrochemical reduction of sulfur in electrolyte systems with moderate polarity ( $\epsilon = 40-45$ ) is carried out in two stages, and in high-polarity ( $\epsilon > 45-50$ ) - in one stage. At the first stage there is an electrochemical reduction of elementary sulfur octet to formation dianion  $\text{S}_8^{2-}$ , at the second stage – reduction of long-chain polysulfides formed as a result of reactions of  $\text{S}_8^{2-}$  disproportionation.

The primary product of electrochemical reduction of sulfur - dianion  $\text{S}_8^{2-}$  is unstable and dissociates with formation of elementary sulfur, polysulfide anions and anion radicals with smaller amount of sulfur atoms. It is suppose that the depth of electrochemical reduction of sulfur at the first stage is determined by stability  $\text{S}_8^{2-}$  which decreases with increasing of the solvents permittivity.

The depth of electrochemical reduction of sulfur at the second stage is determined by the form of existence of lithium polysulfides in electrolyte solutions. Lithium polysulfides existing in electrolyte solutions as contact ion pairs have the greatest electrochemical activity. The form of existence of lithium polysulfides in electrolyte solutions is determined by dimension of solvation sphere of lithium ion, which in for one's turn depends on solvate number of lithium ion, nature of background salt anion, amount of donor atoms in molecules of solvents, molar volume and polarity of the solvents.

The major reason of fast decreasing of sulfur electrode capacity during cycling is the diffusion of sulfur from a positive electrode as lithium polysulfides with formation of electrochemically inactive Li-S immobilized in interstice of a positive electrode and separator, and also on a surface of a negative electrode.

The properties of aprotic dipolar solvents greatest influencing on the cycling of Li-S batteries were determined.