Development of Nanocrystalline Complex Metal Hydrides for Hydrogen Storage

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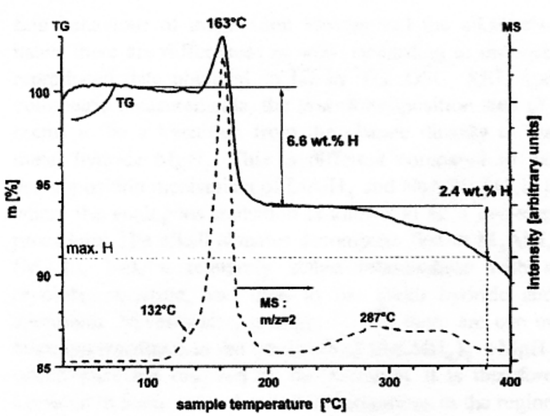
Planned Completion = December 2006

Research Goals and Objectives

- **The objective of this work is to synthesize nanocrystalline Al-Mg alloys which form complex metal hydrides with excellent volumetric hydrogen capacity, low hydrogenation/dehydrogenation temperature, fast kinetics and reasonable gravimetric storage capacity.**
- **The approach to meet the objective includes:**
  - **Use electrodeposition techniques for synthesizing nanocrystalline particles.**
  - **Apply advanced characterization techniques such as x-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM) and nanoindentation to characterize the deposits structure.**
  - **Establish collaboration for the hydrogenation/dehydrogenation characterization.**

Relevance to Current State-of-the-Art

- **Sodium alanate, $NaAlH_4$ is the state-of-the art complex hydride considered as hydrogen storage medium for fuel cells.**
  - **Theoretical capacity of 5.5wt% (practical less than 5wt%)**
  - **Low absorption kinetics**
  - **Reactive with air and moisture**
- **Magnesium alanate:**
  - **Theoretical capacity of 9.3%.**
  - **Mg(AlH4)2 → MgH2 + 2Al + 3H2 (6.6wt% at 163˚C)**
  - **Doping with Ti and ball milling reduced the peak temperature to 120˚C.**



Fichtner M, Fuhr O, Kircher O,"Magnesium alante – a material for reversible hydrogen storage?" J. Alloys and Compounds 356-357:418-422 (2003).

• **Synthesis through methathesis reaction between sodium alanate and magnesium chloride.**

• **No results on kinetics of hydrogen desorption and absorption.**

Relevance to NASA

- Fuel cells are an important part of NASA's future missions.
- Complex hydrides are the most promising source of pure hydrogen for fuel cells.
- There is a need for new materials with high hydrogen capacity, fast kinetics, and low cost.

Budget, Schedule and Deliverables

- **Budget**
  - **2005 funding: 70K**
  - **2006 funding: 31K**
- **Schedule and deliverables**

2005				
	1st quarter	2nd Quarter	3rd Quarter	4th Quarter
Procure and install glove box				
Electrodeposition cell design and fabrication				
Electrolyte design and preparation				
Fabrication of alloys				
Characterization of alloys				

Anticipated Technology End Use

- Electrodeposition is a well established industry and therefore up-scaling of the synthesis technology should be achieved easily.

- It is anticipated that the synthesized powder will be transferred to a high pressure hydrogenation chamber to form magnesium alnate.

- The hydride will be used as a source of hydrogen for fuel cells.

Accomplishments and Results

I. Selection of Electrolyte

- Aqueous based solutions can not be used for deposition of Al or Mg.

Possible Solutions:

1. AlX_3 (X=halogen) in TMPAC (tri-methyl-phenyl-amonium)
2. AlH_3 in DMSO2 (di-methyl-sulfone)
3. AlR_3 (R=Alkyl group) in toluene

After considering different possibilities, we decided that the 3rd option is the best choice.

Electrolytes based on organometallic complexes

- Typically, Alklai metal halides (MX) and Aluminumtrialkyls (AlR_3) are used to form complexes

$MX + AlR_3 \rightarrow M[R_3AlX]$ (1:1 complex)

$MX + 2AlR_3 \rightarrow M[R_3Al\text{-}X\text{-}AlR_3]$ (1:2 complex)

Where, M= Na, K, Rb, Cs
R= Methyl ($-CH_3$), Ethyl ($-C_2H_5$), propyl ($-C_3H_7$), etc.

Lehmkuhl H, Mehler K, Landau U "The principles and techniques of electrolytic aluminum deposition and dissolution in Organoaluminum electrolytes" in *Advances in Electrochemical Science and Engineering*, Vol. 3, Ed. H. Gerischer and C. Tobias, VCH, Weinheim, p. 163 (1994).

Tendency of Complex Formation

- Increases with decreasing the size of the alkyl group:
  methyl(Me)>ethyl(Et)>propyl(Pr)>butyl(Bu)…
- Increases with decreasing the lattice energy of metal halide

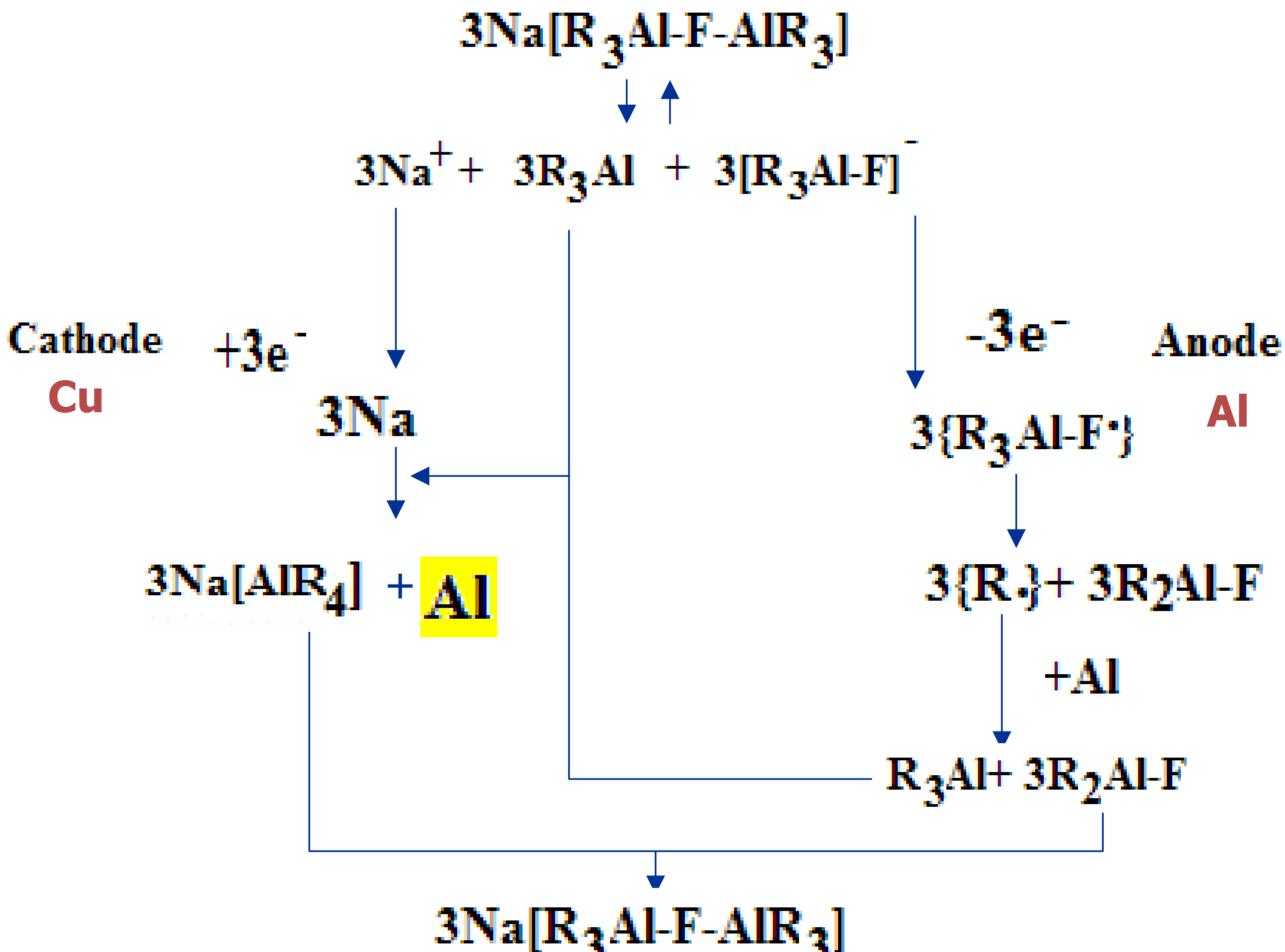
	F^-	Cl^-	Br^-
Na^+	923	787	747
K^+	821	715	682
Rb^+	785	689	660
Cs^+	740	659	631

Lattice Energy (kJ/mol)

Electrolyte Properties

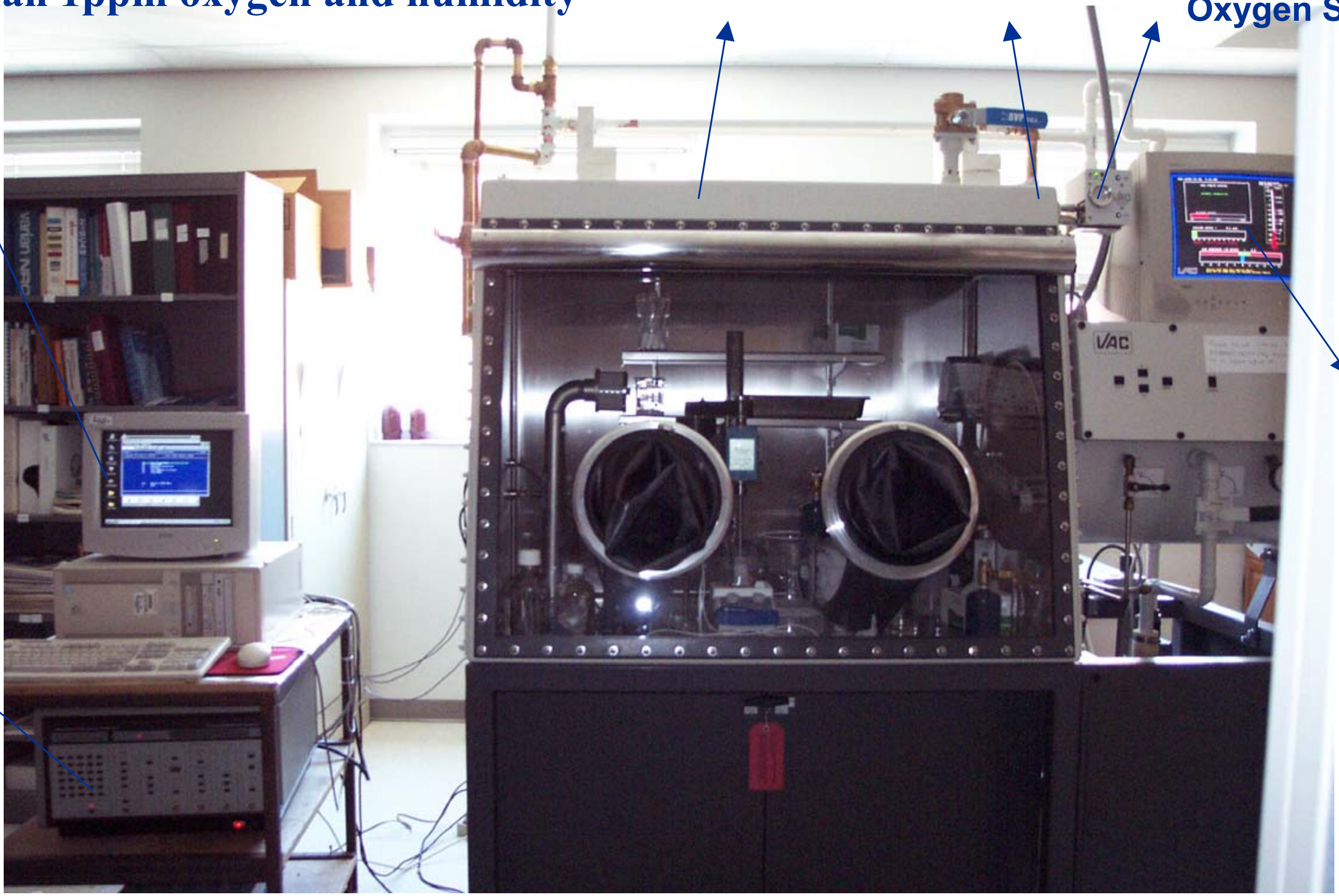
Compound	Melting Point (°C)	Specific Conductivity
$Na[Me_3Al\text{-}F\text{-}AlEt_3]$	65-68	18 (100°C)
$Na[Et_3Al\text{-}F\text{-}AlEt_3]$	35	23 (100°C)
$K[Me_3Al\text{-}F\text{-}AlEt_3]$	135-137	73 (150°C)
$K[Me_3Al\text{-}F\text{-}AlBu_3]$	25	8 (100°C)
$K[Et_3Al\text{-}F\text{-}AlEt_3]$	127-129	73(130°C)

Mechanism of Electrodeposition of Al



II. Procurement and Installation of the glove box

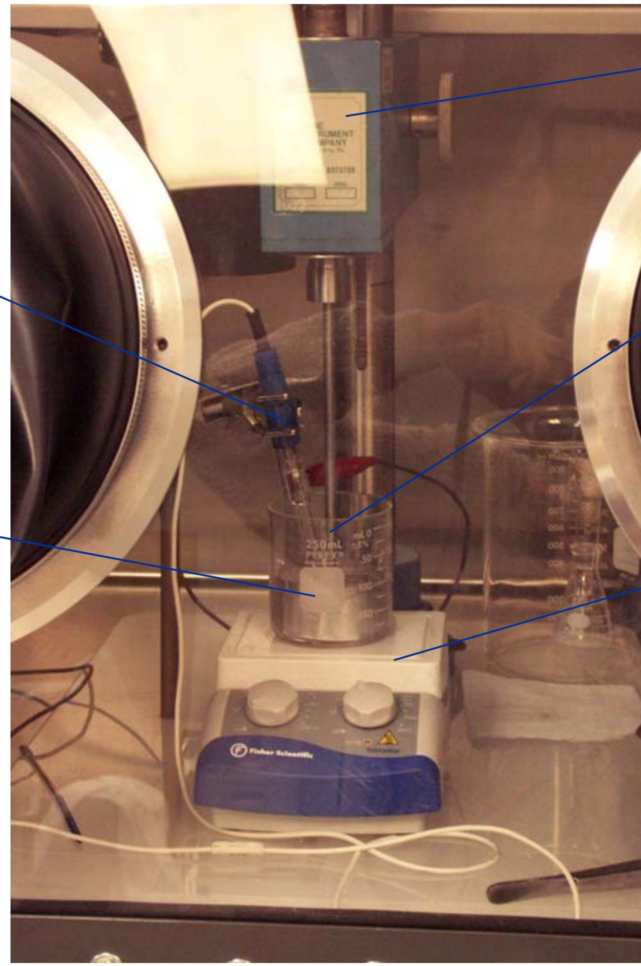
- Less than 1ppm oxygen and humidity



III. Cell Design and Preparation

Ag/AgCl reference electrode in ethylene glycol monobutyl ether + salt bridge containing the electrolyte

Anode made of pure Al and pure Mg

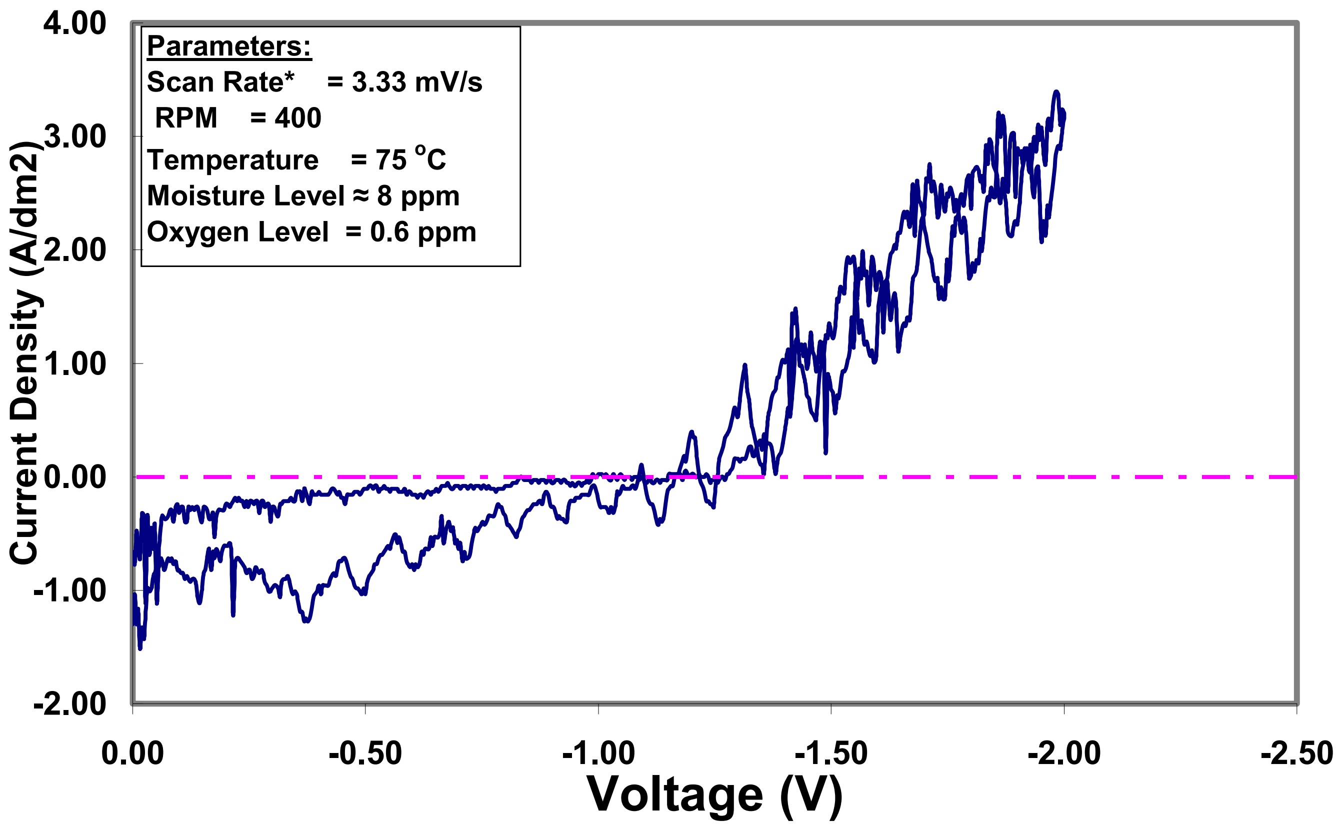


Rotator

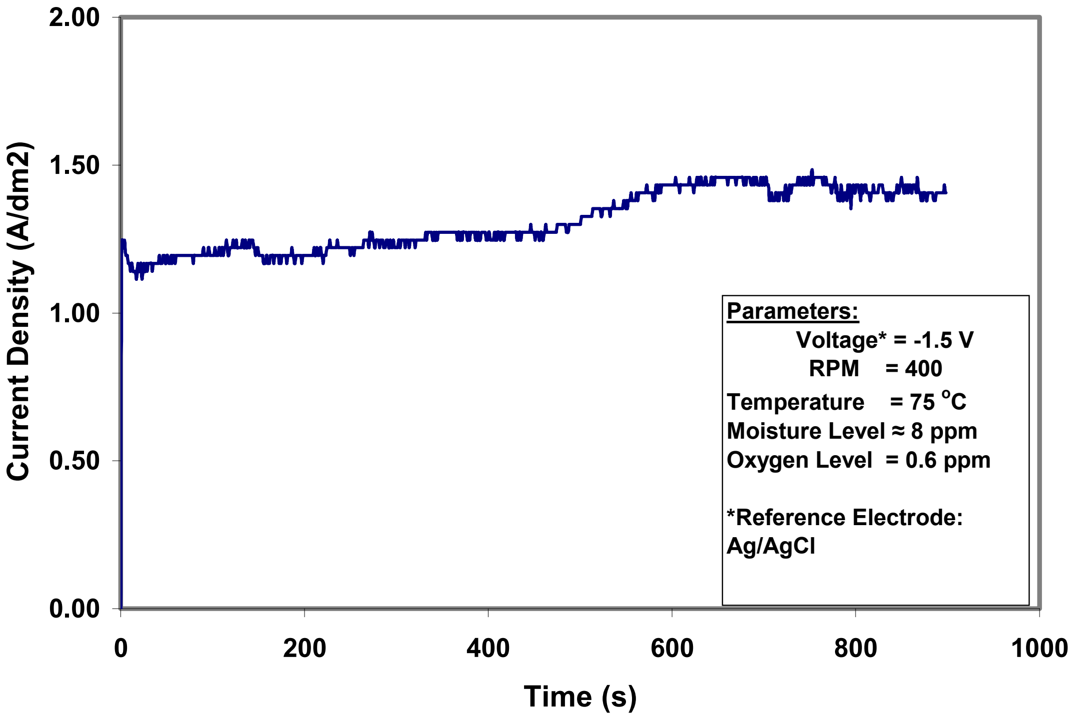
Cathode: copper or graphite cylinder

Heater

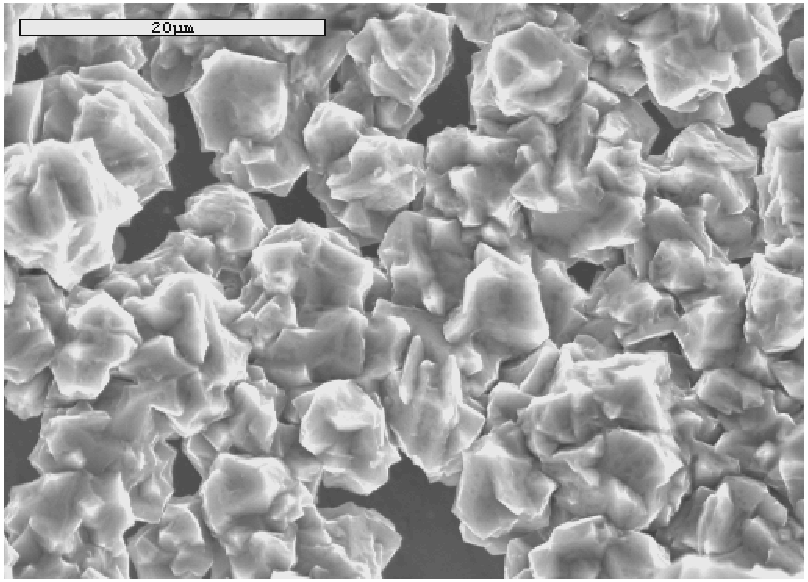
III. Cyclic Voltammetry



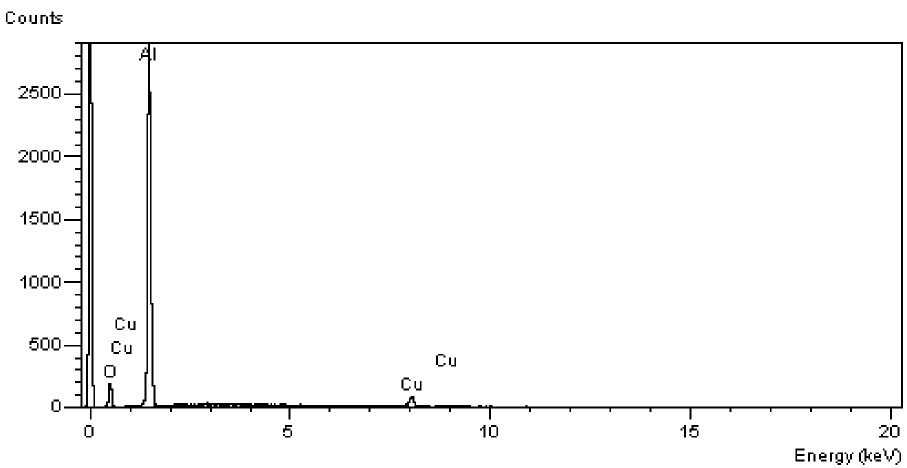
IV. Electrodeposition of aluminum



V. Characterization of the aluminum deposit



SEM



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Future Plans

- We will establish the electrodeposition procedure for Al-Mg alloys during the months of November and December in 2005.

	2006			
	1st quarter	2nd Quarter	3rd Quarter	4th Quarter
Establishing deposition parameters for nanocrystalline Al-Mg alloys				
Establishing conditions for controlling the composition of the alloys				
Structural Characterization of alloys				
Thermal stability				
Hydrogenation/dehydrogenation				