ELECTRODEPOSITION OF SCANDIUM FROM AN IONIC LIQUID SOLUTION

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Abstract

In the present study the electrodeposition of scandium from ionic liquids is researched, as an alternative to high temperature molten salts electrolysis Initially the dissolution of Sc in a form of a chloride salt in the ionic liquid is studied. The solutions prepared are characterized in terms of conductivity and viscosity and the reduction of Sc from the solution prepared is researched by cyclic voltammetry, which showed a cathodic loop at -2.7V vs Fc/Fc+ attributed to Sc reduction. Moreover the solution was used under potentiostatic polarization at -2.9V for a total duration of 24h on an Cu cathode and the deposit was identified by SEM –EDS and XPS analysis and metallic Sc was proved to be electrodeposited.

Introduction

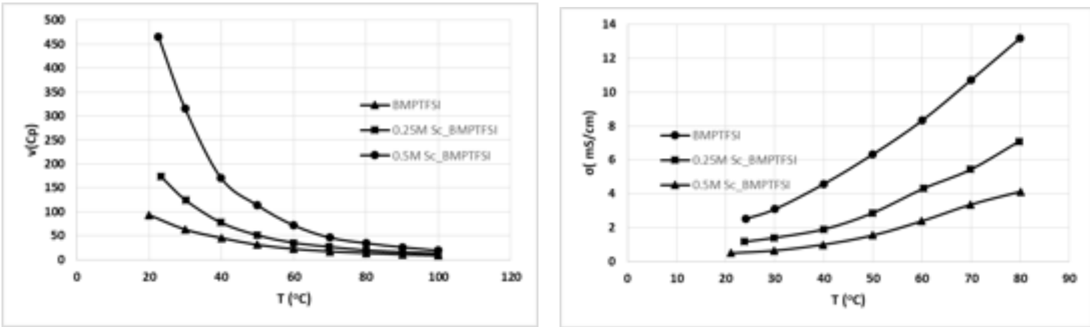
Scandium (Sc) is mainly used in ceramics, lasers, phosphors, and certain high performance alloys for the aerospace industry and is getting increasing attention recently due to its unique properties and its possible applications. One of its most important applications is for preparing Al-Sc alloys. Scandium, with its unique strength and weight-saving characteristics, has been introduced as a potent alloying element in several aluminum alloys (e.g., Al5052 and Al7075) in recent years, bringing about dramatic improvements in their mechanical and physical characteristics. It has been possible to achieve an ideal combination of strength, density, and thermal stability because of the unique precipitation-hardening characteristics of scandium. These alloys are gaining a wide popularity in aeronautical, automotive, and transportation industries. Potential aerospace applications include bulkheads, heat shields, forgings and extrusions for seat tracks, wheels, running gear, and fuel and exhaust systems. Scandium alloys are promising for automotive and air transportation applications because of their capability of weight reduction on critical moving parts. Scandium alloys could also be used in wheels, bumpers, frames, pistons, and airbag canisters. The aluminum scandium welding wire provides a very strong bonding while welding aluminum. This alloy could also be used in the cylinders of diesel engines for power boats. Because of the good corrosion resistance shown by recent studies, scandium alloyed with aluminum could also be used in a saltwater environment (e.g., heat exchanger tubes in desalination plants). Another key use of this alloy is in the manufacturing of various sports equipment, like baseball bats, lacrosse sticks, and bikes .Furthermore Scandium is a key component in producing Solid Oxide Fuel Cells (Scandia-Stabilized-Zirconia solid electrolyte layer) or high strength Aluminum alloys used in 3D printing applications (SCALMALLOY®). Currently Sc, which has high melting point, is obtained by reduction of the fluorides with Ca at 1500 – 1600 ◦C. The reduction is carried out in tantalum crucibles under a protective

Materials and methods

The ionic liquid BMPTFSI was supplied by Iolitec and anhydrous Scandium chloride was purchased by Johnson Matthey. Cyclic voltammetry and chronopotentiometry tests were performed in a three milielectrodes cell (PAR) connected to a VersaSTAT 3 potentiostat (PAR); the obtained experimental data were analyzed with the VersaStudio software (PAR). The working electrode was a platinum disk of d = 1 mm, as a counter electrode a Pt wire immersed directly into the solution was used and finally, as a reference electrode in the cyclic voltammetry a Pt wire was used as a pseudoreference electrode calibrated vs the reversible couple Fc/Fc+. The viscosity of the solutions were measured with a Brookfield DV-I+LV viscometer supplied with an electric thermomantle. The conductivity was measured by a 4 Pt rings electrode conductometer Si-Analytics HandyLab 200. The morphology of electrodeposits was examined by Scanning Electron Microscope (JEOL6380LV), provided with an Energy Dispersive Spectrometer. The XPS core level spectra were analyzed using a fitting routine, which can decompose each spectrum into individual mixed Gaussian-Lorentzian peaks after a Shirley background subtraction

Results - Discussion

The conductivity and the viscosity of the potential electrolyte were studied at various temperatures. Fig.1a presents the results for the viscosity measurements performed for solutions of 0.5M, 0.25M [Sc] and for the pure ionic liquid BMPTFSI. It was shown that the more concentrated solutions present higher viscosity. 0.5 M solution, as it was anticipated, present significant viscosity, while the dilute solution 0.25 M at room temperature is almost 5 times less viscous than the concentrated one. The conductivity measurements were realized for the concentrated solution (0.5 M) and the dilute one (0.25 M) and for the pure ionic liquid BMPTFSI and the results are presented in Fig.1 and demonstrate that at room temperature the conductivity of the two solutions is totally comparable. However, as temperature is increased above 30oC, the less concentrated solutions of 0.25M exhibit slightly higher conductivity in comparison to the 0.5M solution. Nevertheless, both solutions present significantly reduced conductivity in comparison to the pure ionic liquid, due to the high viscosity they present.



(a) **(b)**

Figure 1: (a) Viscosity measurements vs T (b) Conductivity measurements vs T

The solution of BMPTFSI with dissolved 0.5M ScCl3was studied in terms of cyclic voltammetry. The purpose was to investigate if the reduction of scandium could occur from the solution produced. The cyclic voltammogramm was recorded at room temperature with a scan rate of 20 mV/s on a Pt working electrode vs Fc/Fc+ reversible couple. The electrochemical window of the ionic liquid had been defined in the same conditions. The cyclic voltommagramm revealed that when the potential was scanned at negative values after -2V a reductive current was generated with a reduction peak at -2.6V that was attributed to the reduction of trivalent scandium cations to the zerovalent state (Fig.2). Due to the absence of a corresponding anodic peak the reduction was considered as an irreversible reaction.

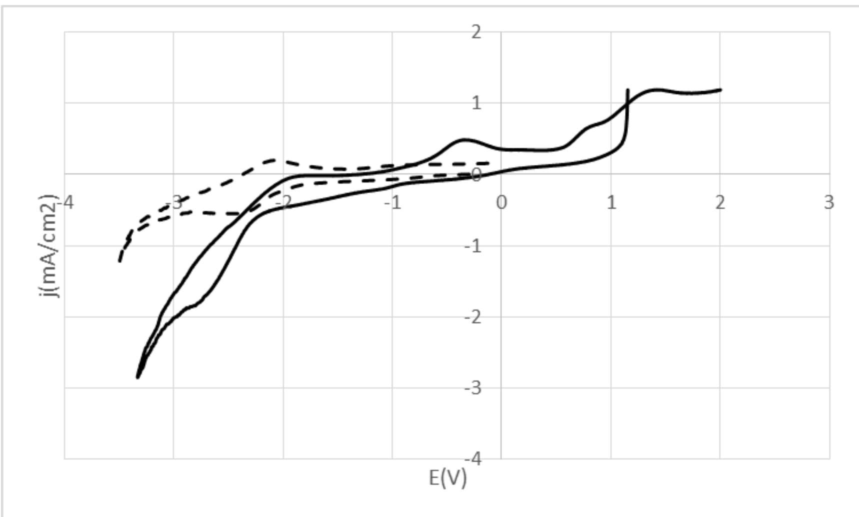


Figure 2: Cyclic voltammogramm of 0.5M ScCl3 BMPTFSI (solid line) and cyclic voltammetry of BMPTFSI ionic liquid (dash line).

The solution was used under potentiostatic polarization at -2.9V for a total duration of 24h in order to investigate Scelectrodeposition. As a working electrode a Cu sheet of $1cm^2$ was used and as a reference electrode, a Pt pseudoreference calibrated vs Fc/Fc+was employed. The cell operation current was stabilized after the first five hours at -20μA, while the cell voltage was set stable after the first two hours at almost 3.5V. After the end of electrolysis, the working electrode was examined by XPS analysis to determine whether metallic Sc has been electrodeposited. Sputtering cycles by the bombardment of Ar ions were used. Sputtering causes the appearance of a peak assigned to Sc^0. During sputtering the Sc_2O_3 removed and as the sputtering time increases the Sc^0 appeared (Fig. 3).

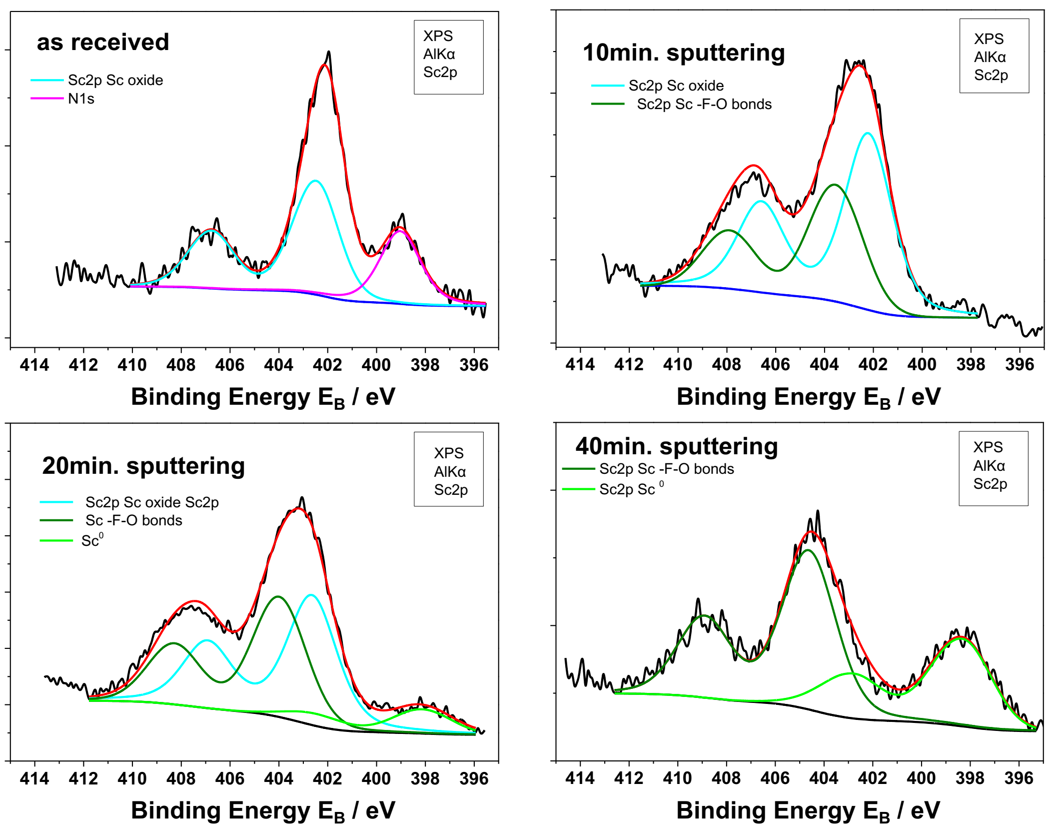
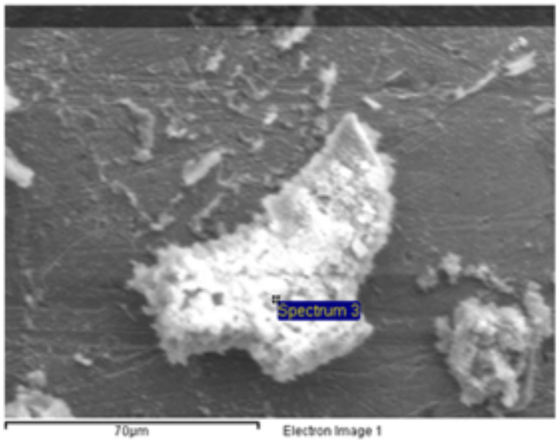
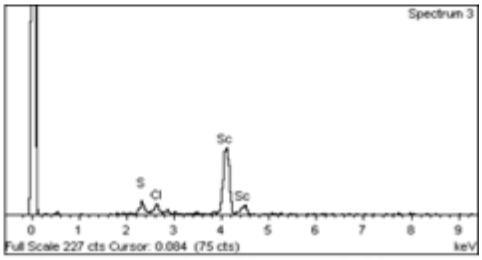


Figure 3: XPS core level spectra of Sc2p-N1s combined window of the as received and sputtered sample.

Subsequently, the deposit was submitted to SEM-EDS. The SEM analysis showed that the deposit was spongy and presented cracks probably due to its quick and uncontrolled oxidation. The EDS spectra confirmed the XPS findings showing important amounts of Sc and O2 since the deposit was oxidized by contacting air and small impurities of S. The existence of S in the deposit is justified by the inadequate removal of the electrolyte (Fig. 4).





Element	Weight%	Atomic%
S K	5.82	7.85
Cl K	5.63	6.88
Sc K	88.55	85.27
Totals	100.00	

Figure 4: SEM image of the deposit and the EDS spectra

Conclusions

BMPTFSI seems to be a promising ionic liquid. The dissolution of Sc salts in the specific ionic liquid was tested and it was achieved to dissolve directly in the ionic liquid high amounts of ScCl3. The electrolyte produced was studied in terms of viscosity, conductivity and cyclic voltammetry was performed that revealed the reduction of Sc cations. Potentiostatic electrolysis was performed and Sc was detected in the form of metallic Sc.

Acknowledgments

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