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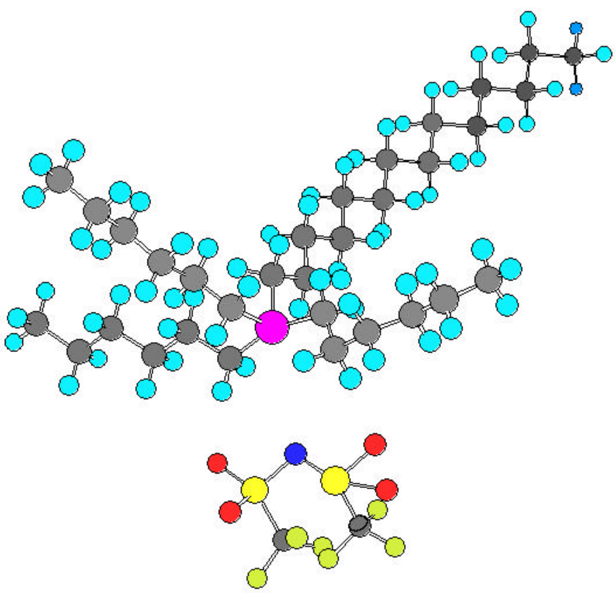
CYPHOS® IL 109

Phosphonium Ionic Liquid



Introduction:

Why consider a “phosphonium” ionic liquid?

Soon after the discovery that certain nitrogen based room temperature liquid salts were found to be useful as battery electrolytes (1a,1b,), interest in these and similar salts as novel fluids and solvents developed. There were a scant number of papers during the 1980s and early 1990s but mainly due to the efforts of the group at The Queen’s University – Belfast, headed up by Professor Ken Seddon, there has been an exponential rise in interest and number of publications in the last 7 to 8 years. (2) Indeed, almost an entire issue of Green Chemistry (3) has been devoted to ionic liquids.

Perhaps one of the most influential publications to direct industrial attention to ionic liquids was a feature article entitled “Designer Solvents” in C&E News – March 30,1998 in which Ken Seddon, Robin Rogers, Tom Welton, Helene Olivier and others elaborated on the potential of ionic liquids. While the article dealt almost entirely with nitrogen based ionic liquids, there was a brief reference by Ken Seddon which alluded to the fact that phosphonium salts are also a potential source of numerous ionic liquids. This brief reference to phosphonium ionic liquids is very much representative of the current fraction of publications relating to phosphonium based ionic liquids. With the exception of several papers and patents by George Parshall in the mid 1970s using stannate and germanate salts and John Knifton et al in the early 1990s which centre on the use of molten tetrabutylphosphonium bromide as an ionic solvent, almost the entire volume of ionic liquid literature deals with nitrogen based systems and in particular, those based on 2-methylimidazolium salts.

There was a good reason for the lack of phosphonium based ionic liquid publications – availability of the starting material! While Cytec has been commercially producing phosphine derivatives since 1971, it was not until 1990 that tributylphosphine was produced on a large commercial scale. Since that time, not only has tetrabutylphosphonium chloride and bromide become available in multi ton scales, many other trialkylphosphines and the corresponding quaternary phosphonium salts are or can be manufactured on a large scale.

The phosphonium cation contains four substituents and the various combinations along with the multitude of various available anions represents an enormous number of possible salts. Even when one restricts the cation to the generic formula – $[PR_3R']^+$, the number is still very large. Of course, not all such phosphonium salts are liquid at room temperature, but by a judicious selection of R and R’ as well as the appropriate anion, there are many phosphonium salts which are in fact liquid at room temperature and many more which fall within the broad general definition of ionic liquids as salts which are low melting – that is less than 100 °C.

There are several reasons why one might consider a phosphonium ionic liquid. The most important one for those contemplating an industrial process is availability and cost. Phosphonium salts can meet both of these demands – already Cytec is manufacturing phosphonium salts on a multi ton scale and because of the high volumes, costs will be relatively low. For commercial products, chemical inventory registration is also part of the availability equation. While, most of the possible phosphonium ionic liquids are still not registered, several are already listed on EINECS, TSCA, EEC, AICS, PICCS and DSL.

Ionic liquids, in general, are not going to be outrageously expensive, but they will not be in the same league as toluene, 2-hydroxypropane (IPA) or tetrahydrofuran (THF). This means that to be economically viable, they must be chemically as well as thermally very stable for multiple recycle use. Even 0.5 to 1% decomposition can lead to major losses after 10 to 20 cycles. Not only will there be solvent losses but there will also be contamination of the ionic liquid solvent and/or products with decomposition byproducts.

In this regard, phosphonium salts are much more thermally stable than the corresponding ammonium salts and even have an edge on imidazolium salts. This is very important for processes which operate at temperatures greater than 100 °C. In addition to being slightly less thermally stable, the imidazolium cation contains protons which are not entirely inert. They are some what acidic which can result in carbene formation. Phosphonium salts, on the other hand have no such acidic protons.

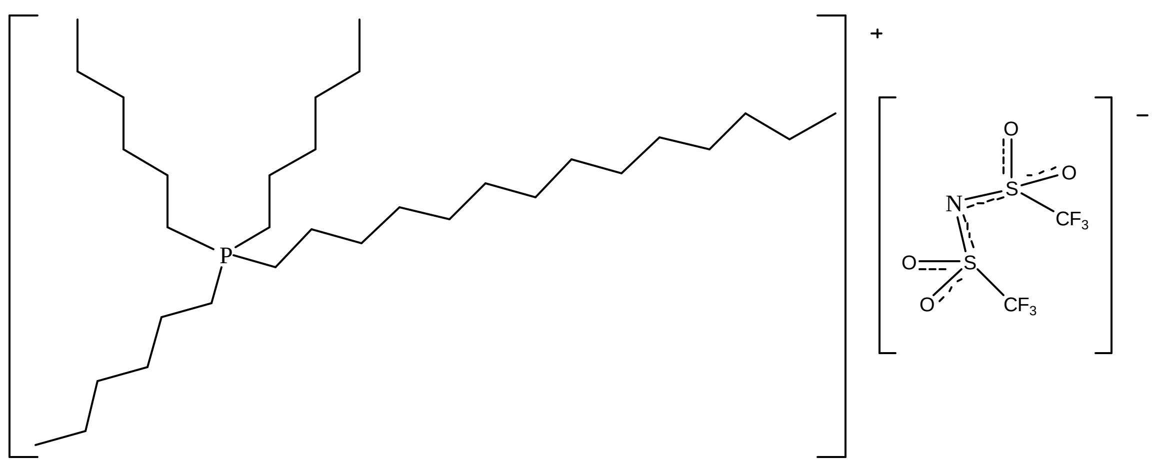
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

Trade Name: **CYPHOS IL 109 phosphonium ionic liquid**

Chemical Name: tetradecyl(trihexyl)phosphonium bistriflamide

C.A.S. Number: [460092-03-9]

Registration: None



CYPHOS IL 109 phosphonium ionic liquid is a low viscosity ionic liquid prepared via a metathesis route from the corresponding chloride salt.(4) Consequently, although essentially chloride free, the normal synthesis will leave approximately 0.1% chloride in the product.

Miscibility:

CYPHOS IL 109 is one of the most hydrophobic phosphonium ionic liquids. It will form biphasic mixtures with water and when fully saturated, the water content is only 0.7%. CYPHOS IL 109 is miscible with most common organic solvents such as those listed in Table 1.

Table 1

CYPHOS IL 109 Miscibility

Diluent	Miscible
water	No
hexane	Yes
toluene	Yes
2-hydroxypropane (IPA)	Yes
diethylether	Yes
tetrahydrofuran	Yes
dichloromethane	Yes

Viscosity:

The viscosity is relatively low (Figure 1) and is dramatically lowered even further by the addition of reactants and or reaction products as simulated by the addition of toluene or hexane in Figure 2.

Thermal Stability:

Typically standard TGA plots are used to determine relative thermal stability of ionic liquids. Heating rates of 5 to 10 °C per minute either under an inert atmosphere or under oxidative conditions such as air are usually reported. Under these conditions, the onset for weight loss for CYPHOS IL 109 is approximately 390 and 310 °C under dinitrogen and air respectively. (Figure 3). However, in reality, the true temperature at which an ionic liquid is thermally stable is much lower. Figures 4 and 5 are isothermal TGA plots under dinitrogen and air respectively. The respective safe operating temperatures would appear to be 210 and 180 °C.

Electrochemical Window:

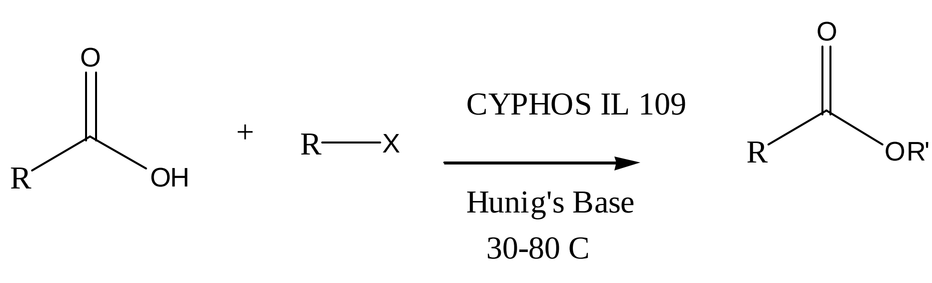
Phosphonium ionic liquids are noted for their wide electrochemical windows. A cyclic voltammogram for CYPHOS IL 109 is given in Figure 6. (7)The very stable tetraalkylphosphonium ion is not reduced until -3.0 volts, whereas oxidation at the anodic limit does not occur until +2.5 volts. The total electrochemical window is thus 5.5 volts. (4) This window is at least 0.5 V wider than corresponding imidazolium salts. It is expected that in general, the cathodic limit for most phosphonium salts will remain relatively constant at -3.0 volts and the anodic limit will be dependant on the oxidative potential of the anion.

Applications:

CYPHOS IL 109 is an especially useful solvent for catalytic Friedal-Crafts alkylations and acylations (5, 6). CYPHOS IL 109can also be used to carry out stoichiometric nitrations of arenes using only a slight excess of fuming nitric/sulfuric acid. (8)

Bio-transformations are often limited to the concentration of either the substrate or products due to toxicity effects on either the enzymes or organisms. For example, 1500 mg/l of phenol is toxic to Pseudomonas putida. However, the bio-degradation can be carried out in a two phase system such as CYPHOS IL 109/(aqueous phenol), in which the phenol will partition into the IL phase at a concentration which is non-toxic to P. putita. This organism is totally compatible with CYPHOS IL 109 and is thus able to consume the phenol from the aqueous phase as it gradually partitions into the IL phase (10).

CYPHOS IL 109 has been successfully used as a solvent for high yield esterification of carboxylic acids with alkylhalides under very mild conditions (9).



The esterification proceeds well when using promary, secondary or tertiary alkylhalides and potassium carbonate has been shown to be a successful substitute foe

Hunig's base. In conventional solvents, esterification with tertiary alkylhalides generally fails.

Analysis:

An assay procedure for CYPHOS IL 109 is currently under development. However, it is expected to assay > 97%. Because it is prepared via a metathesis route from the corresponding chloride salt, it is expected that it will contain up to 0.1% chloride ion. In addition, it will normally contain about 0.1% water.

The chloride content can be readily determined by titration with standardized $AgNO_3$ in a 75% 2-hydroxypropane (IPA) water medium. Karl-Fischer titration is adequate to determine residual water.

^{31}P NMR is generally not suitable for precise analysis. However, the distinctive signal at +33 ppm can be useful for qualitative analysis.

While electrospray mass spectral analysis (ESMS) is generally not available in every laboratory, this also a very useful tool for both quantitative and qualitative analysis.

LC/MS is the most universal tool to identify and quantify cations and anions (11).

References:

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1b Fannin, A. A. Jr; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; and Williams, J. L., J. Phys. Chem. 1984, **88**, 2614-2621

2) "Forward", Professor Ken Seddon, Green Chemistry April, 2002.

3) Green Chemistry April, 2002

4) "Industrial Preparation of Phosphonium Ionic Liquids"; Christine Bradaric, Andrew Downard, Christine Kennedy, Allan Robertson, Yuehui Zhou; Green Chemistry, 2003, **5**, 143-152

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6) "Metal bistriflamide compounds & methods for synthesis of metal bistriflamide compounds"; Martyn Earle, Barry McAuley, Alwar Ramani, Jillian Thompson, Kenneth Seddon; WO 2002/072260

7) Private communication from Alwar Ramani – The Queen's University, Belfast

8) Private communication from Alwar Ramani – The Queen's University, Belfast

9) "A mild esterification process in phosphonium salt ionic liquid"; J McNulty, A Cheekoori, J J Nair, V Larichev, A Capretta and A Robertson; Tet. Lett., 2005, **46**, 3641-3644

10) "Phosphonium ionic liquids for degradation of phenol in a two-phase partioning bioreactor"; Environmental Biotechnology; 2005, 67, 131-137; M.D. Baumann, A.J. Daugulis and P.G. Jessop

11) “Development of an LC/MS Analytical Procedure for Ionic Liquids with Emphasis on Phosphonium Ionic Liquids”; 1st International Congress on Ionic Liquids, June 19-22, 2005, Salzburg, Austria; T.T. Chang and M.J. Piquette

(also posted on www.cytec.com/business/phosphine)

Figure 1

CYPHOS IL 109 – Viscosity vs. Temperature

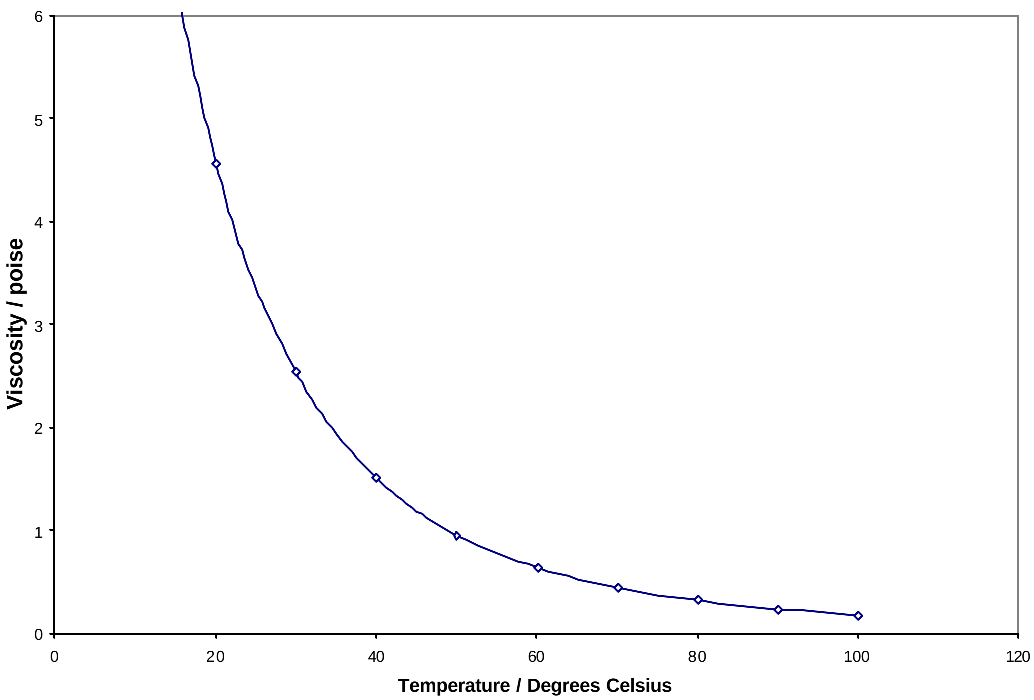


Figure 2

CYPHOS IL 109 – Effect of Solute on Viscosity

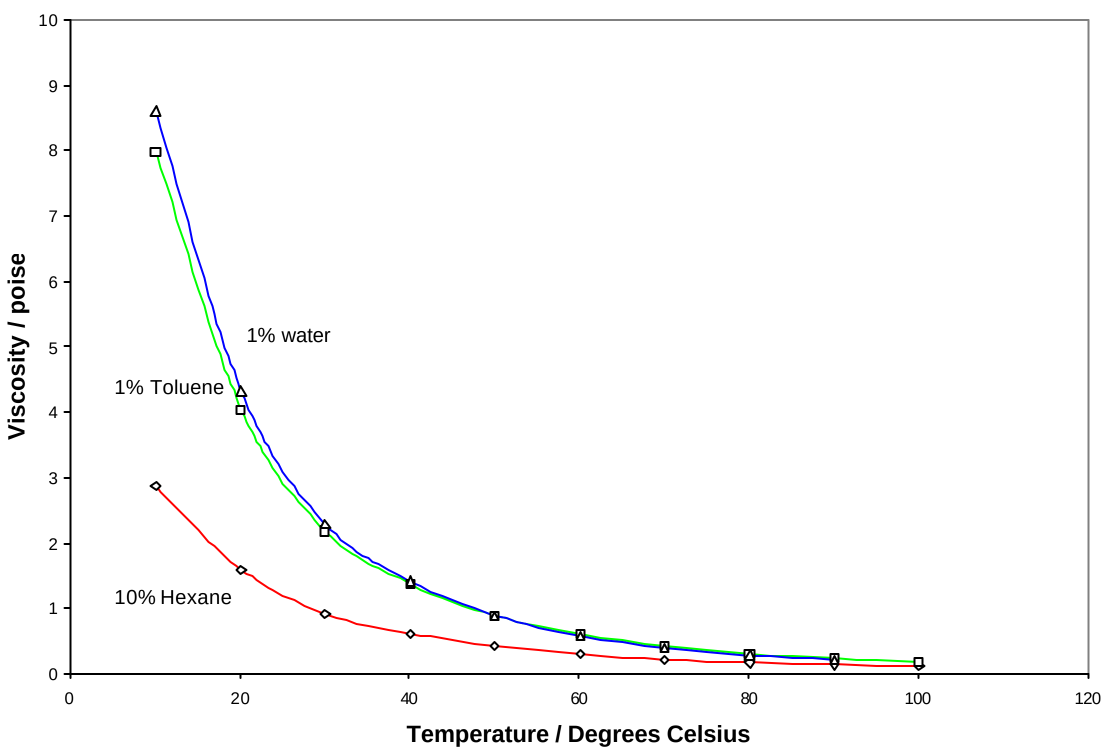


Figure 3

CYPHOS IL 109 – Standard TGA Plots under Air and N_2

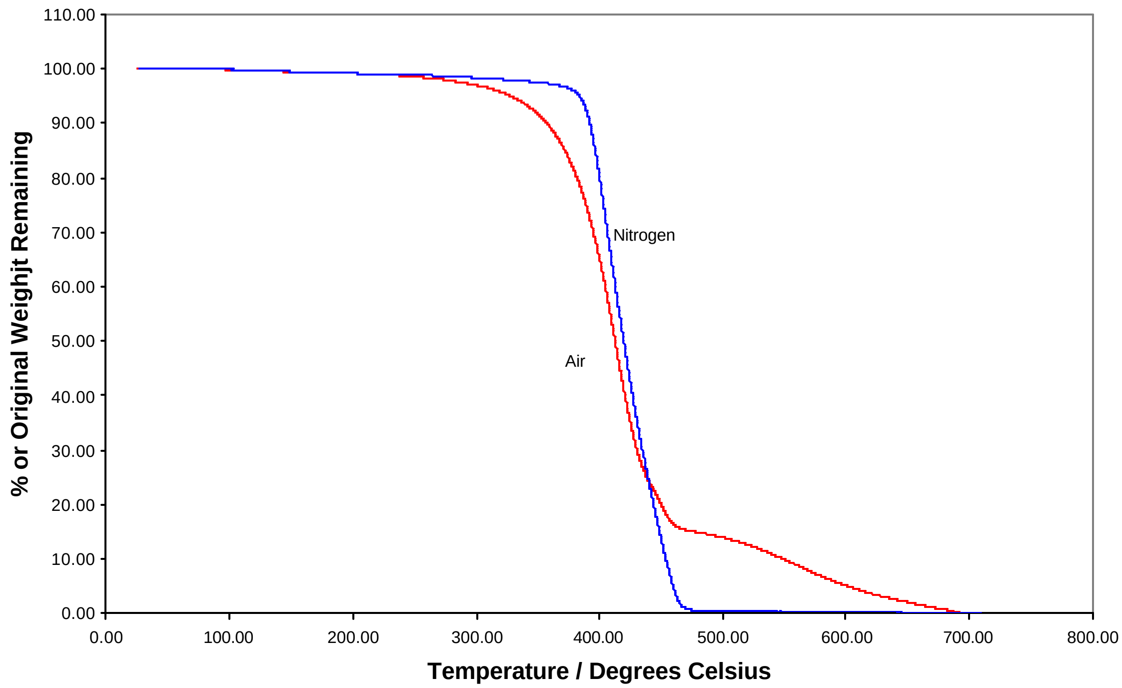


Figure 4

CYPHOS IL 109 – Isothermal TGA Plots under Air

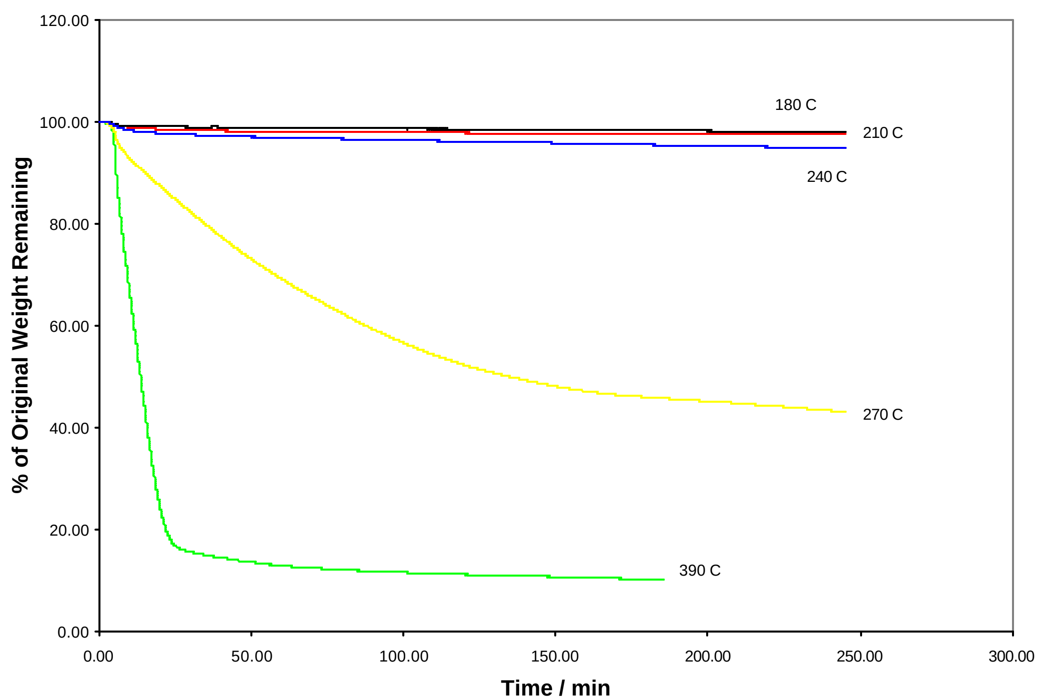


Figure 5

CYPHOS IL 109 – Isothermal TGA Plots under N_2

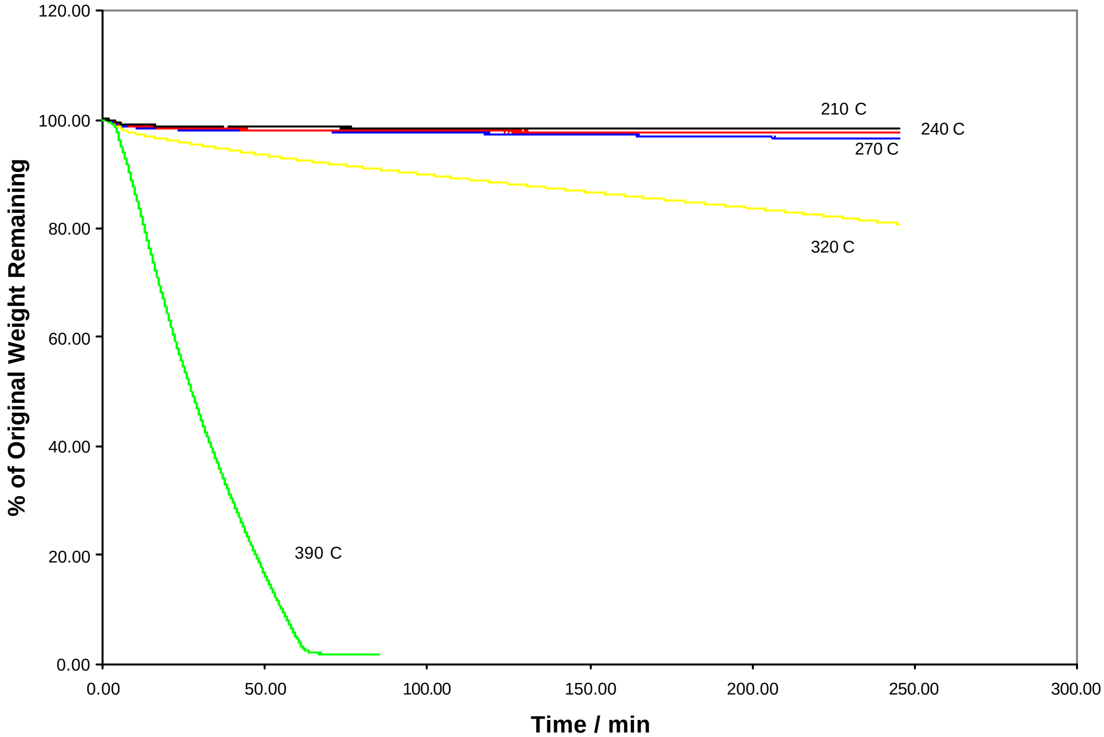
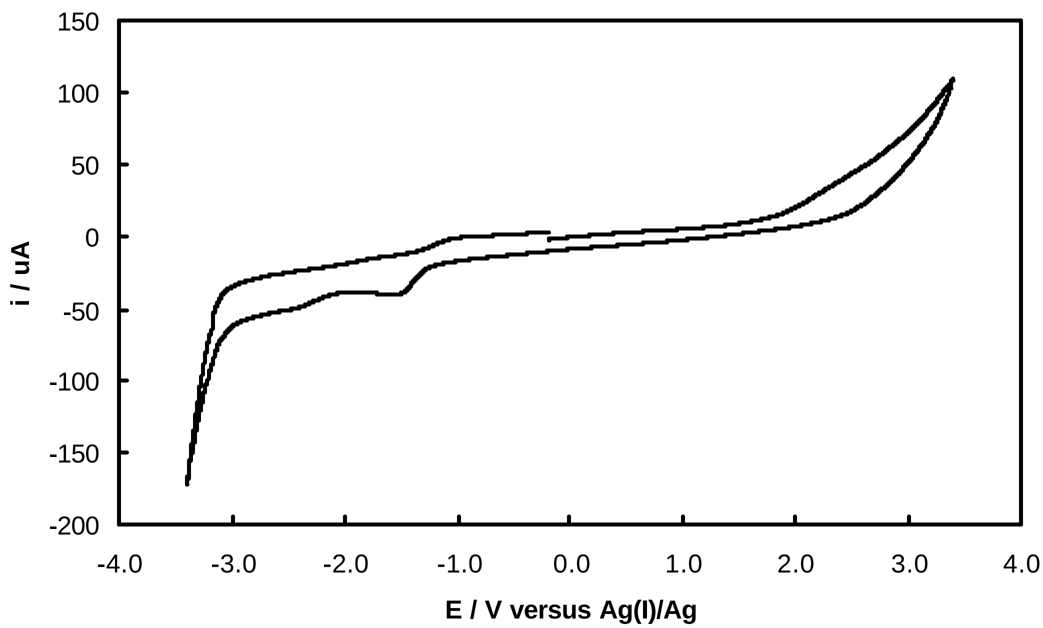


Figure 6

CYPHOS IL 109 – Electrochemical Window



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