(12) **UK Patent** (19) **GB** (11) **2566473** (13) **B**

(45) Date of B Publication **04.03.2020**

(54) Title of the Invention: Magnesium salts

(51) INT CL: ***C07C 31/32*** (2006.01) ***C07C 29/68*** (2006.01) ***C07F 5/06*** (2006.01) ***H01M 10/054*** (2010.01)
H01M 10/0568 (2010.01)

(21) Application No:	**1714771.1**
(22) Date of Filing:	**14.09.2017**
(43) Date of A Publication	**20.03.2019**

(56) Documents Cited:

GB 2128604 A	**GB 1402544 A**
DE 004227720 A1	**US 3761500 A1**

Inorganica, Chimica Acta, Vol. 29, 1978, Mehrotra, R. C. et al, "Preparation and characterization of some volatile double isopropoxides of aluminum with alkaline earth metals", pp. 131-136

(58) Field of Search:
As for published application 2566473 A viz:
INT CL **C07C, C07F**
Other: **WPI, EPODOC, CAS ONLINE**
updated as appropriate

Additional Fields
Other: **None**

(72) Inventor(s):
Evan Keyzer
Jeongjae Lee
Clare Grey
Dominic Wright

(73) Proprietor(s):
Dyson Technology Limited
Tetbury Hill, Malmesbury, Wiltshire, SN16 0RP,
United Kingdom

(74) Agent and/or Address for Service:
Dyson Technology Limited
Intellectual Property Department, Tetbury Hill,
MALMESBURY, Wiltshire, SN16 0RP, United Kingdom

GB 2566473 B

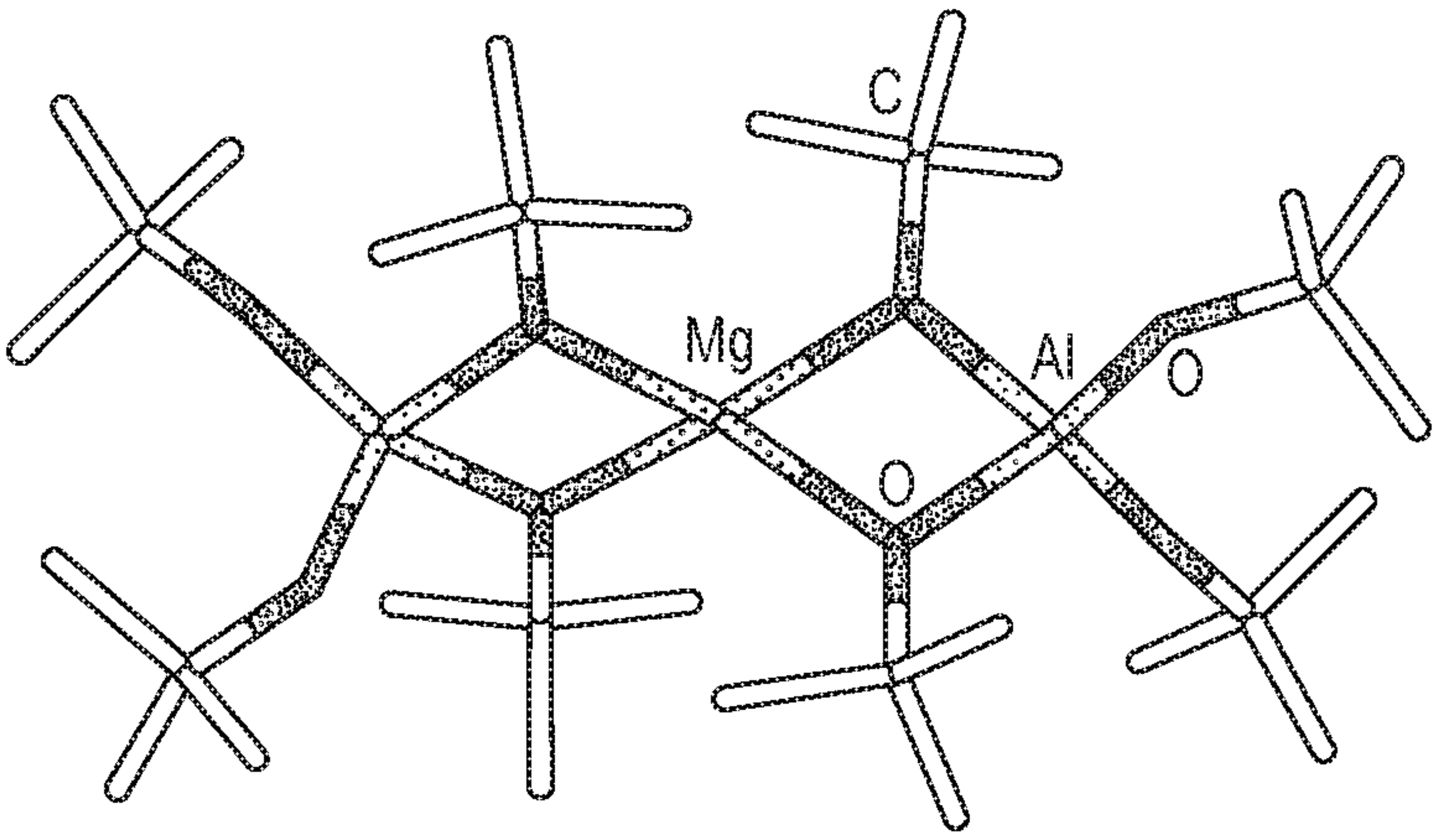


FIG. 1

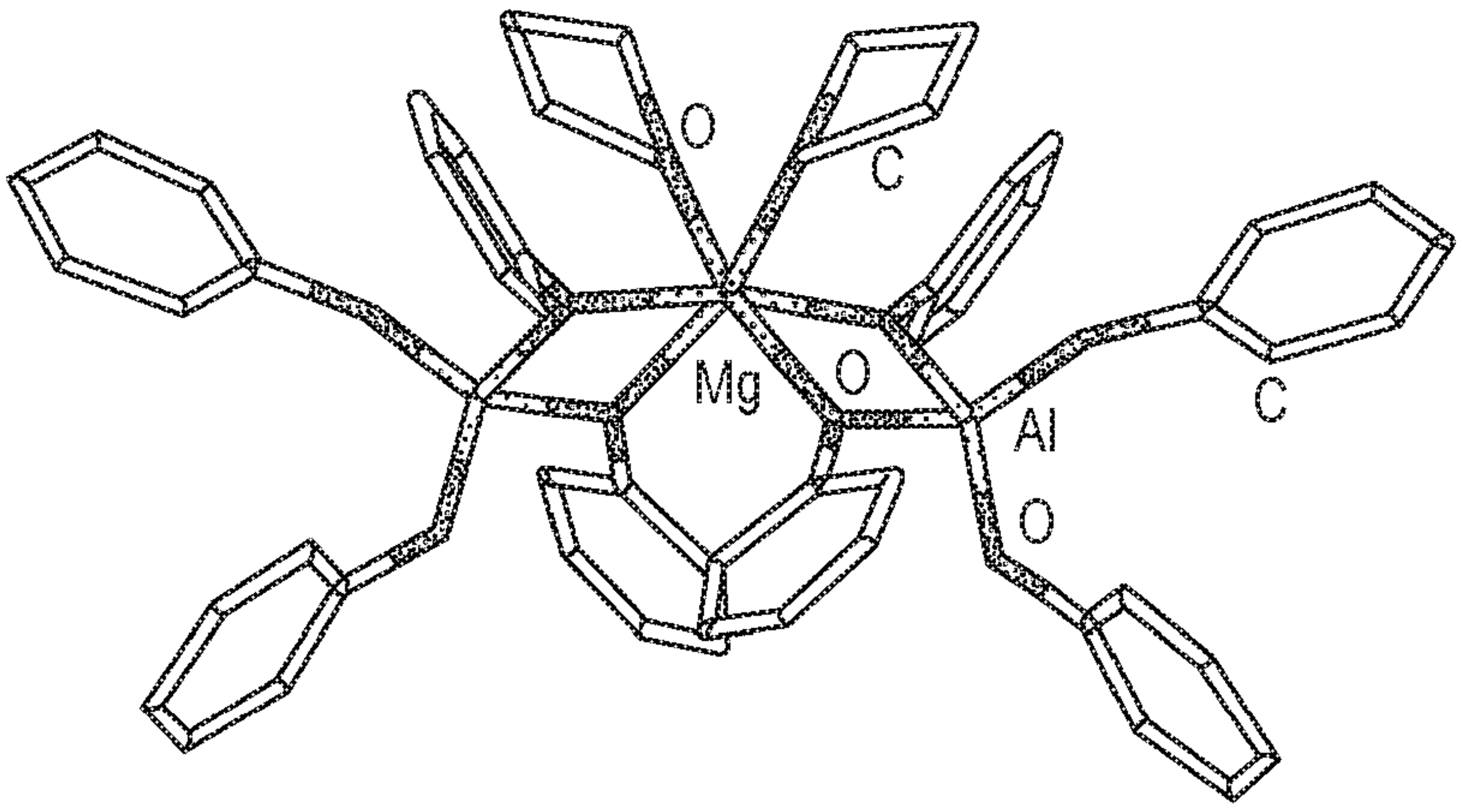


FIG. 2

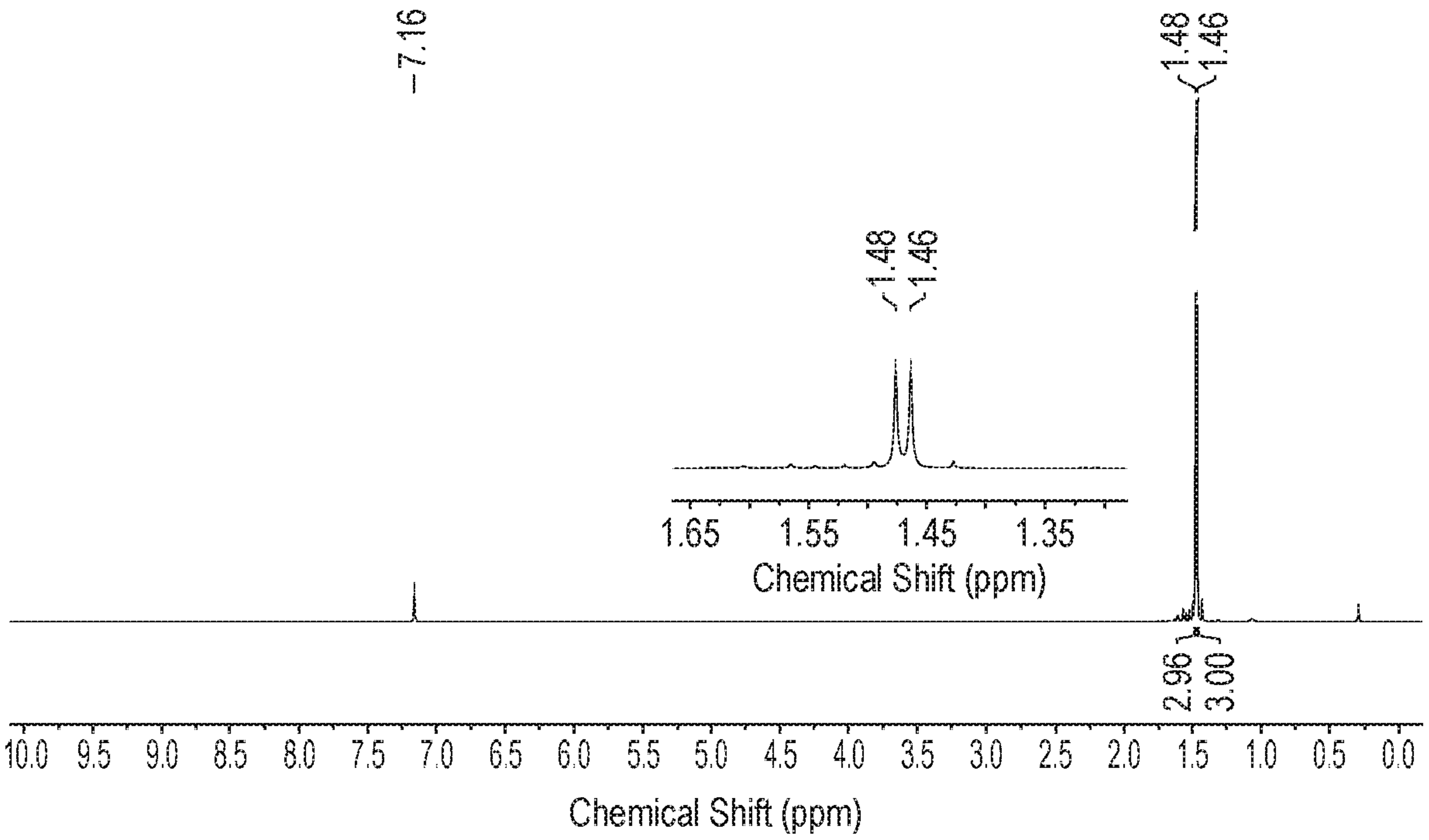

7.16
1.48
1.46
1.48
1.46
1.65
1.55
1.45
1.35
Chemical Shift (ppm)
2.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

FIG. 3

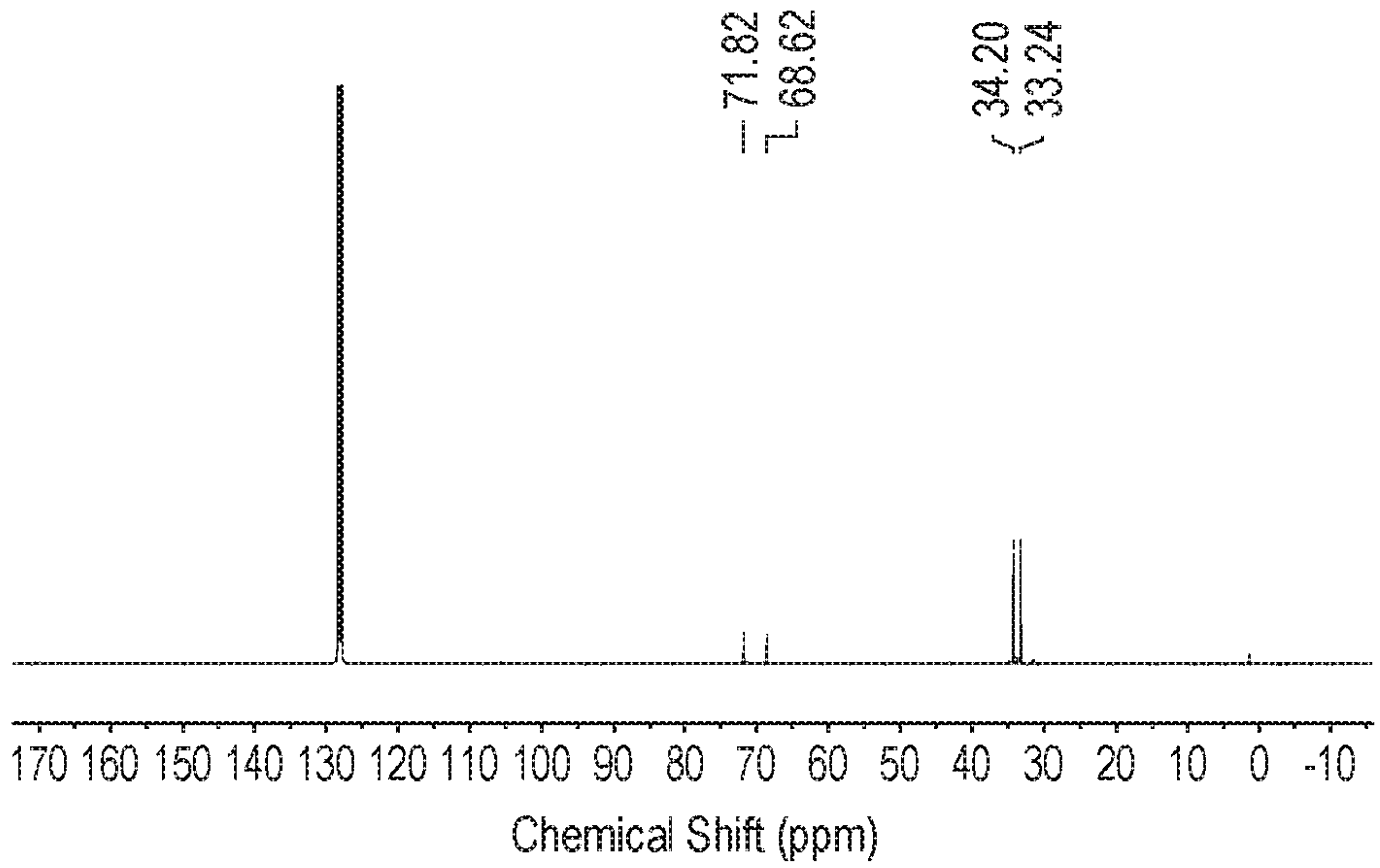

71.82
68.62
34.20
33.24
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

FIG. 4

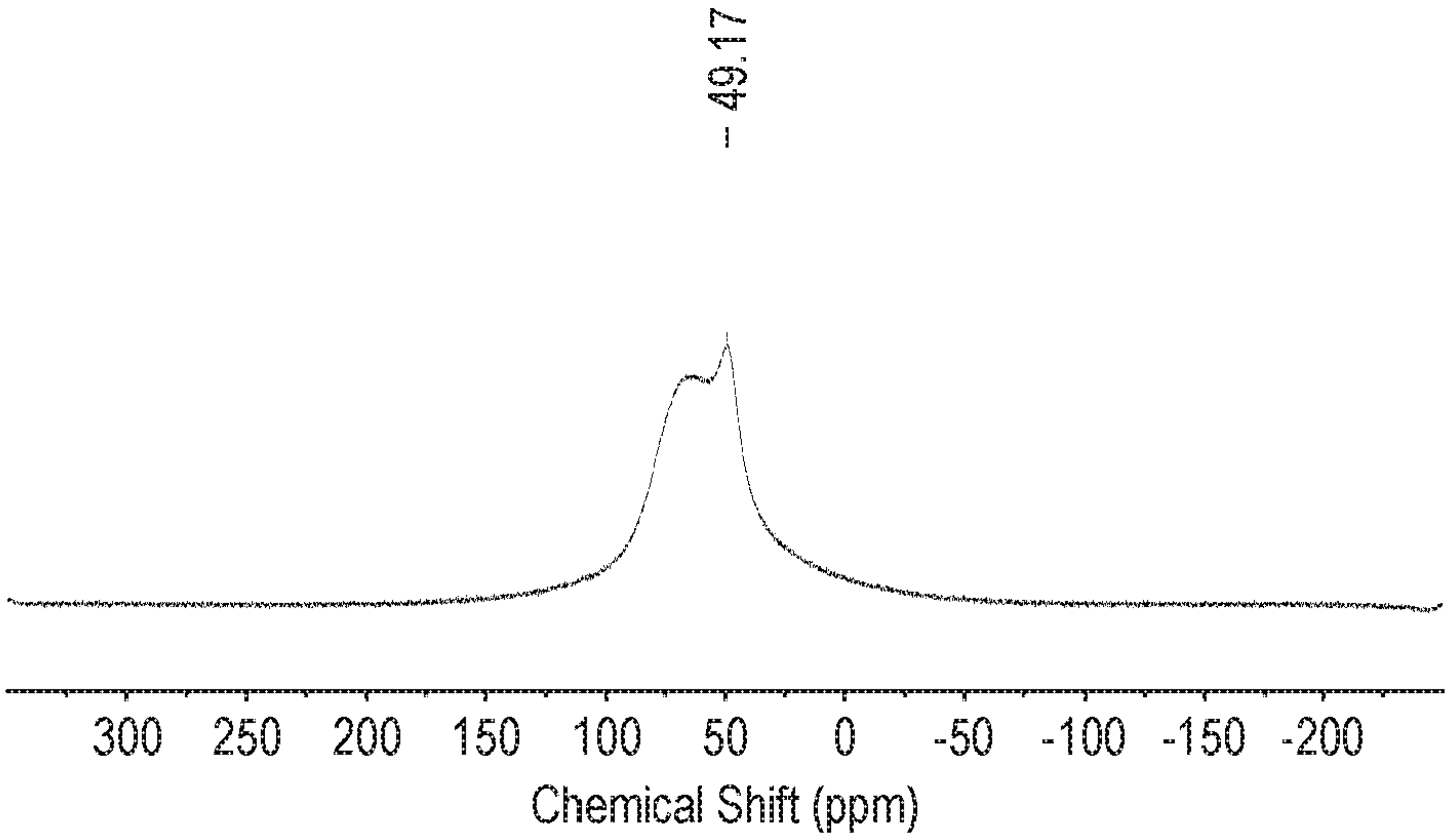

49.17
300
250
200
150
100
50
0
-50
-100
-150
-200
Chemical Shift (ppm)

FIG. 5

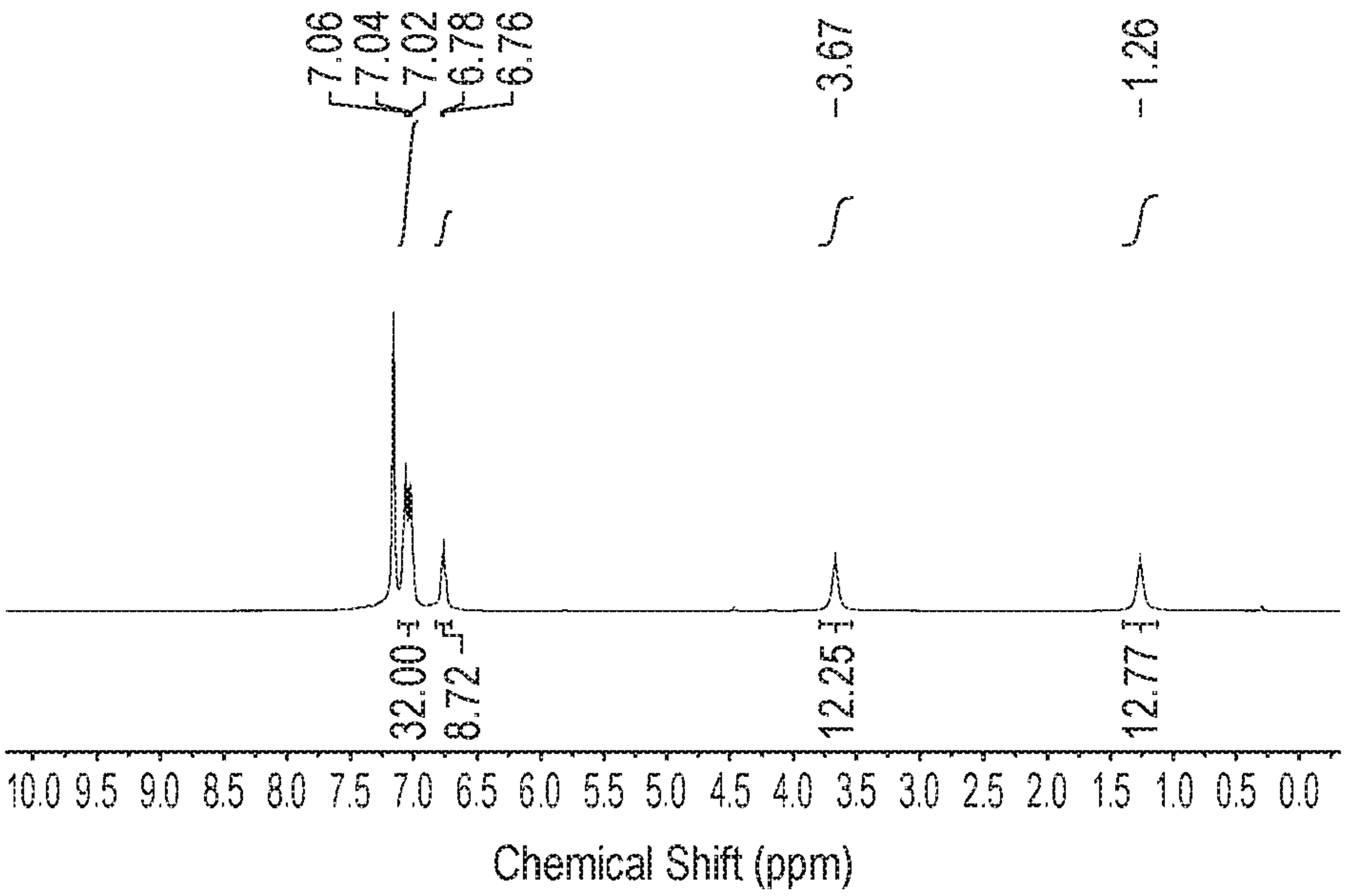

7.06
7.04
7.02
6.78
6.76
3.67
1.26
32.00
8.72
12.25
12.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

FIG. 6

18 10 18

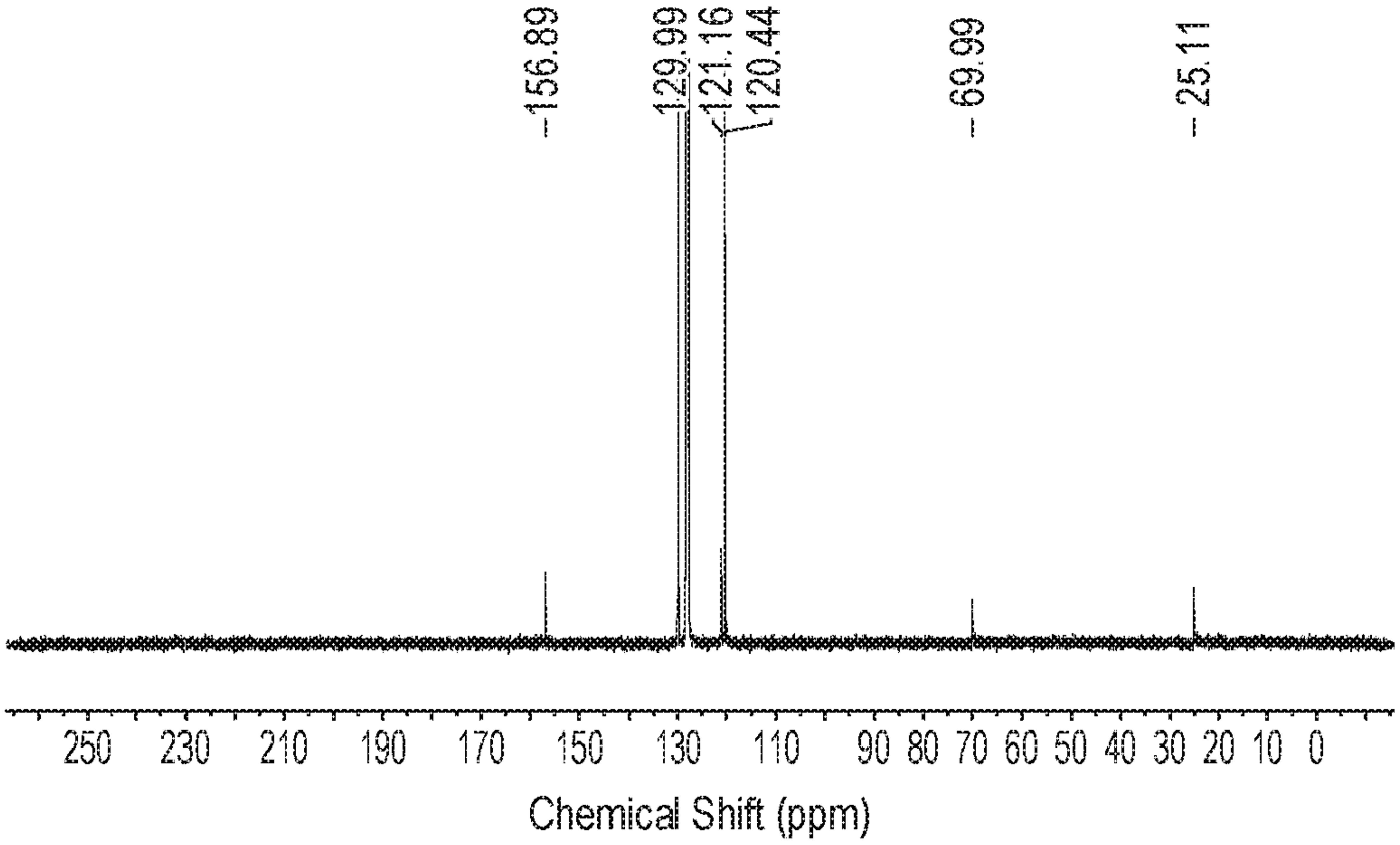


FIG. 7

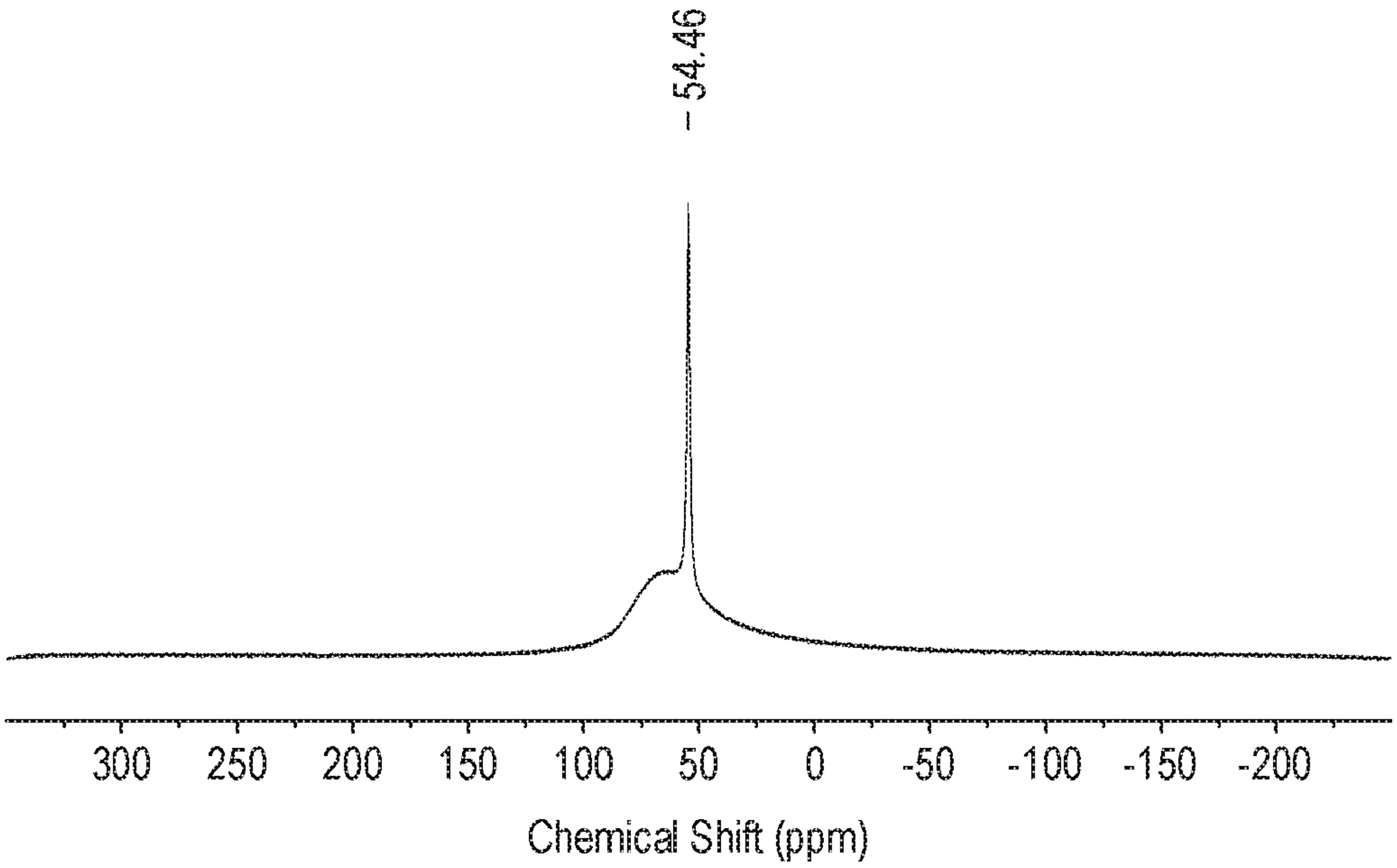


FIG. 8

18 10 18

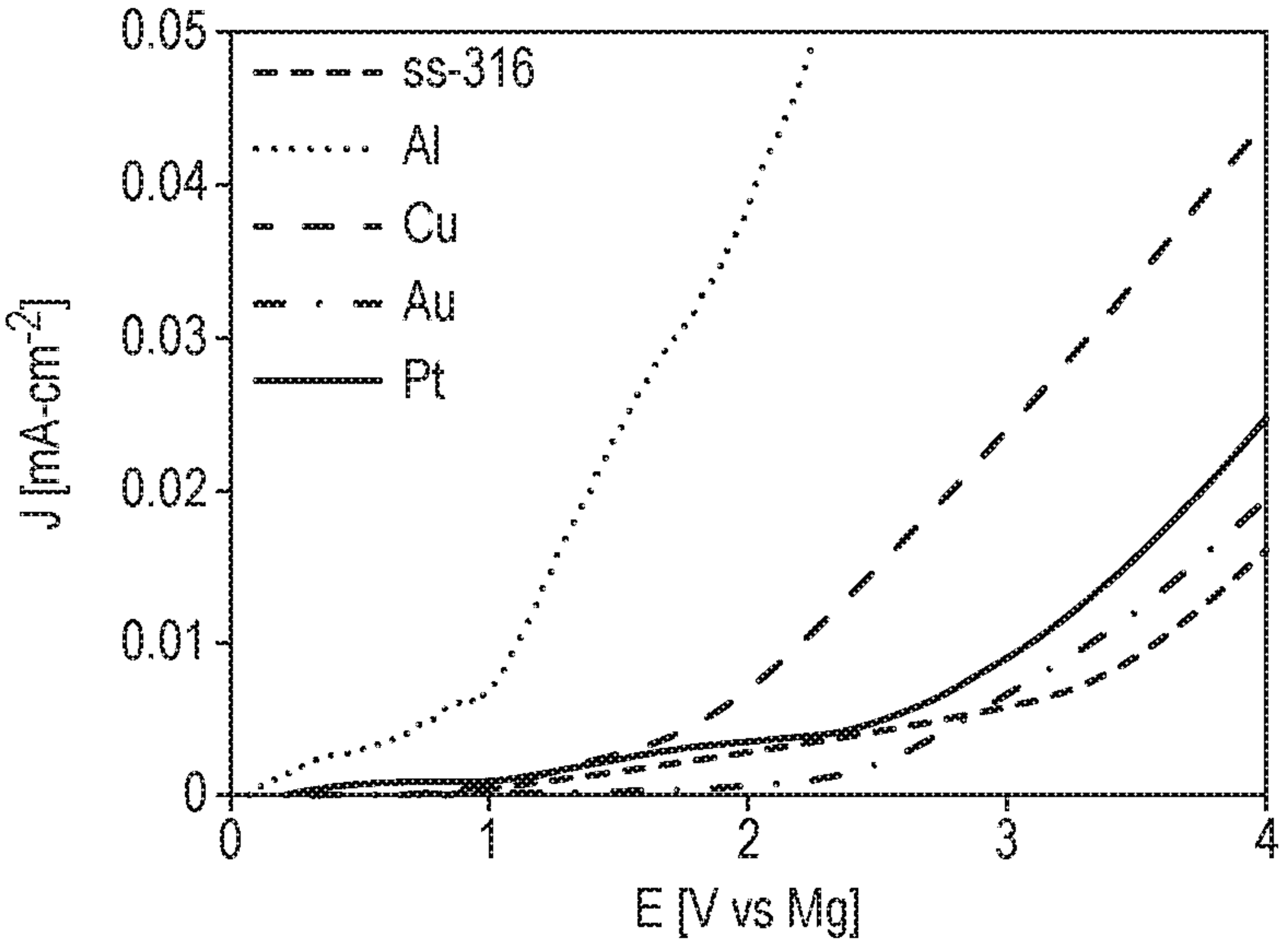


FIG. 9

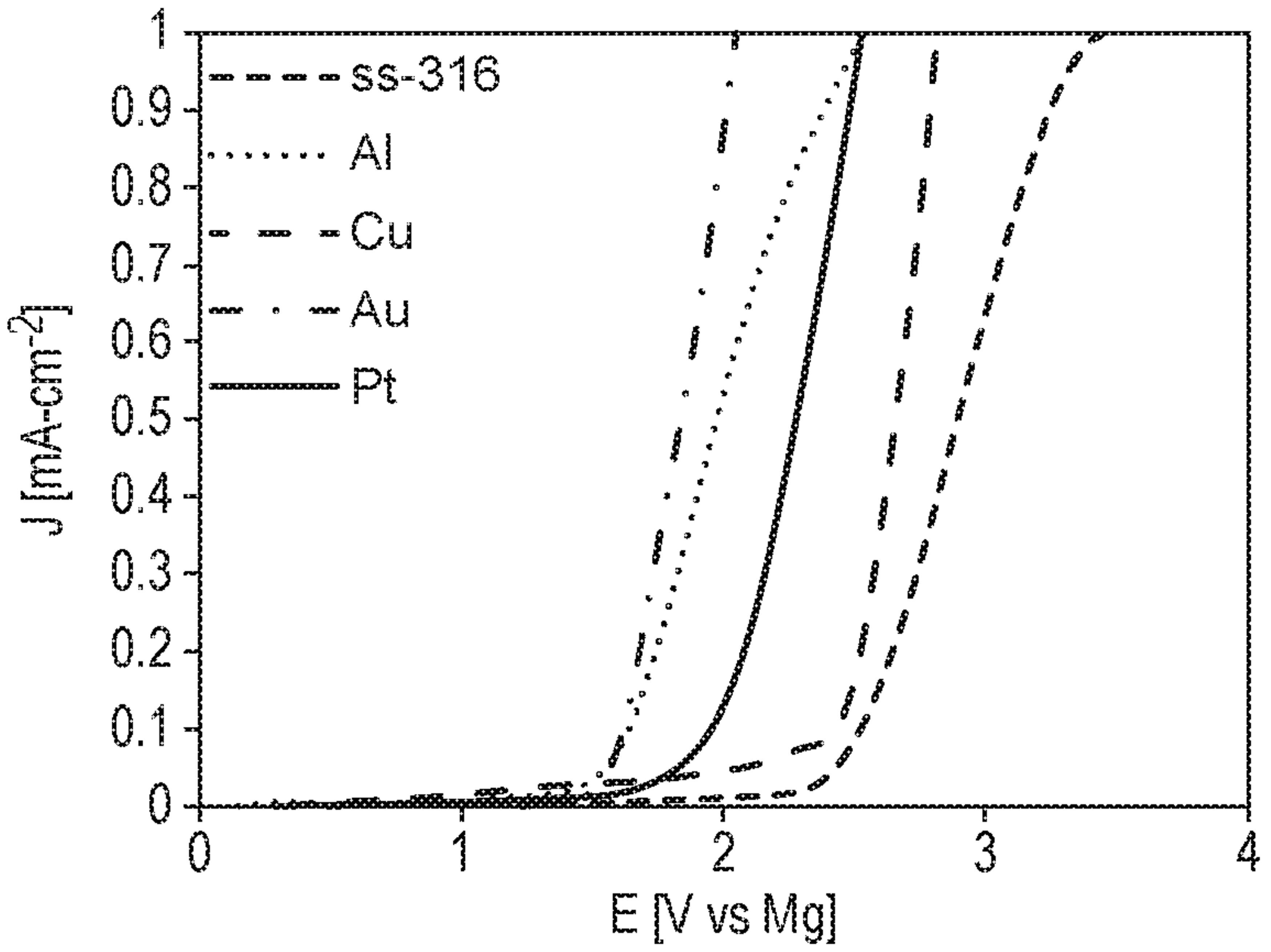


FIG. 10

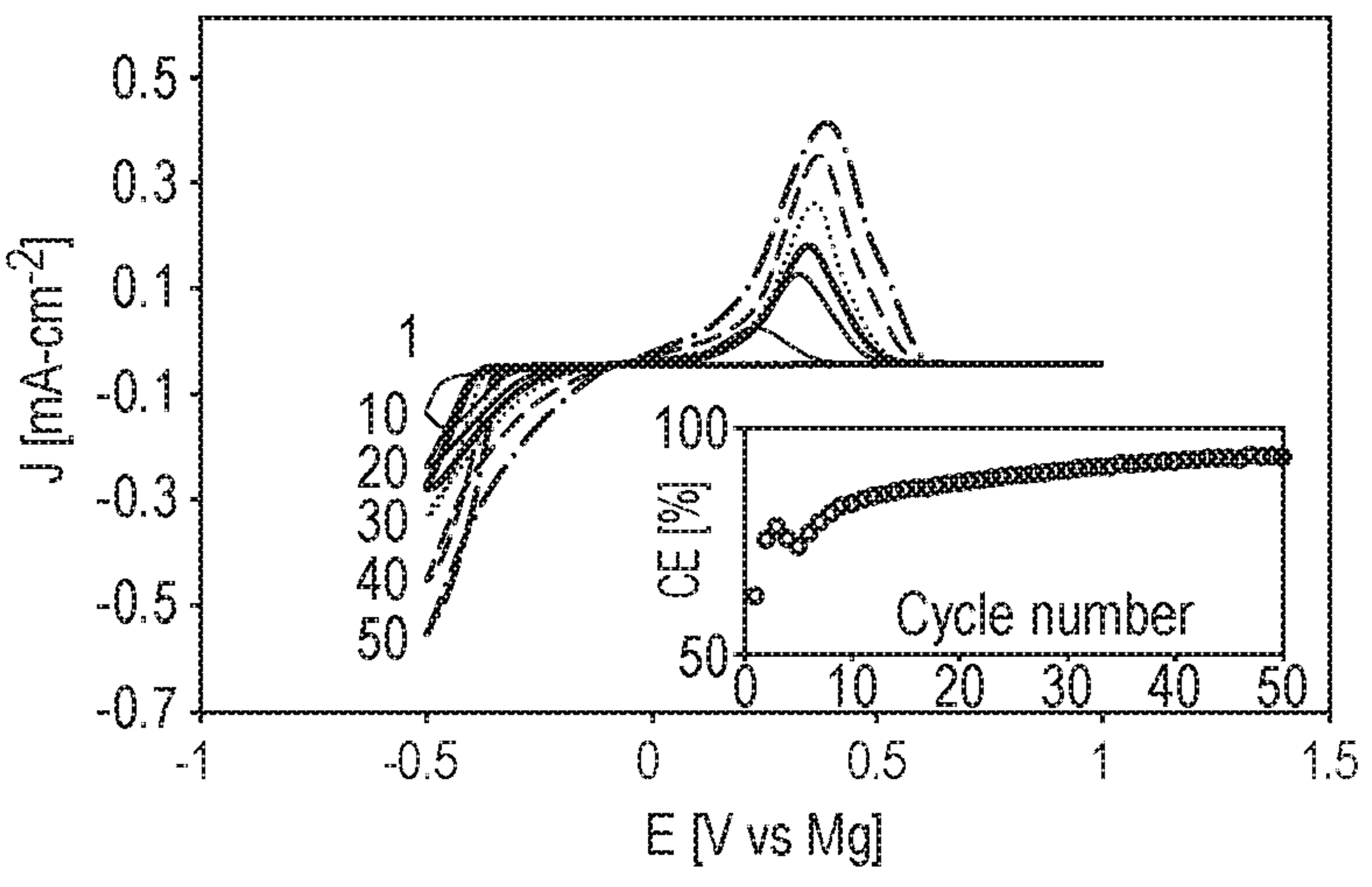


FIG. 11

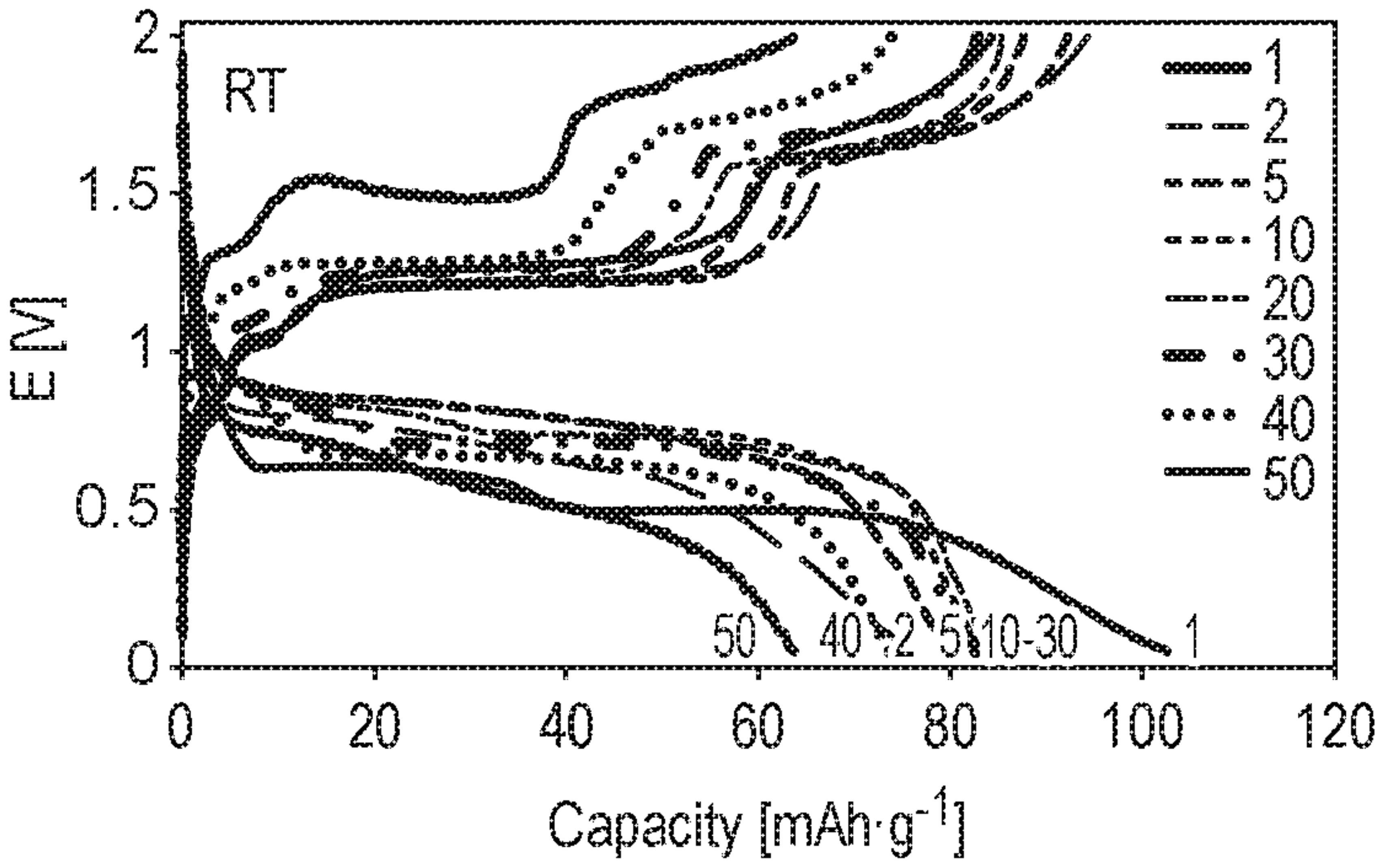

RT
E [V]
Capacity [mAh·g^{-1}]
0
0.5
1
1.5
2
0
20
40
60
80
100
120
1
2
5
10
20
30
40
50
50
40
2
5
10-30
1

FIG. 12

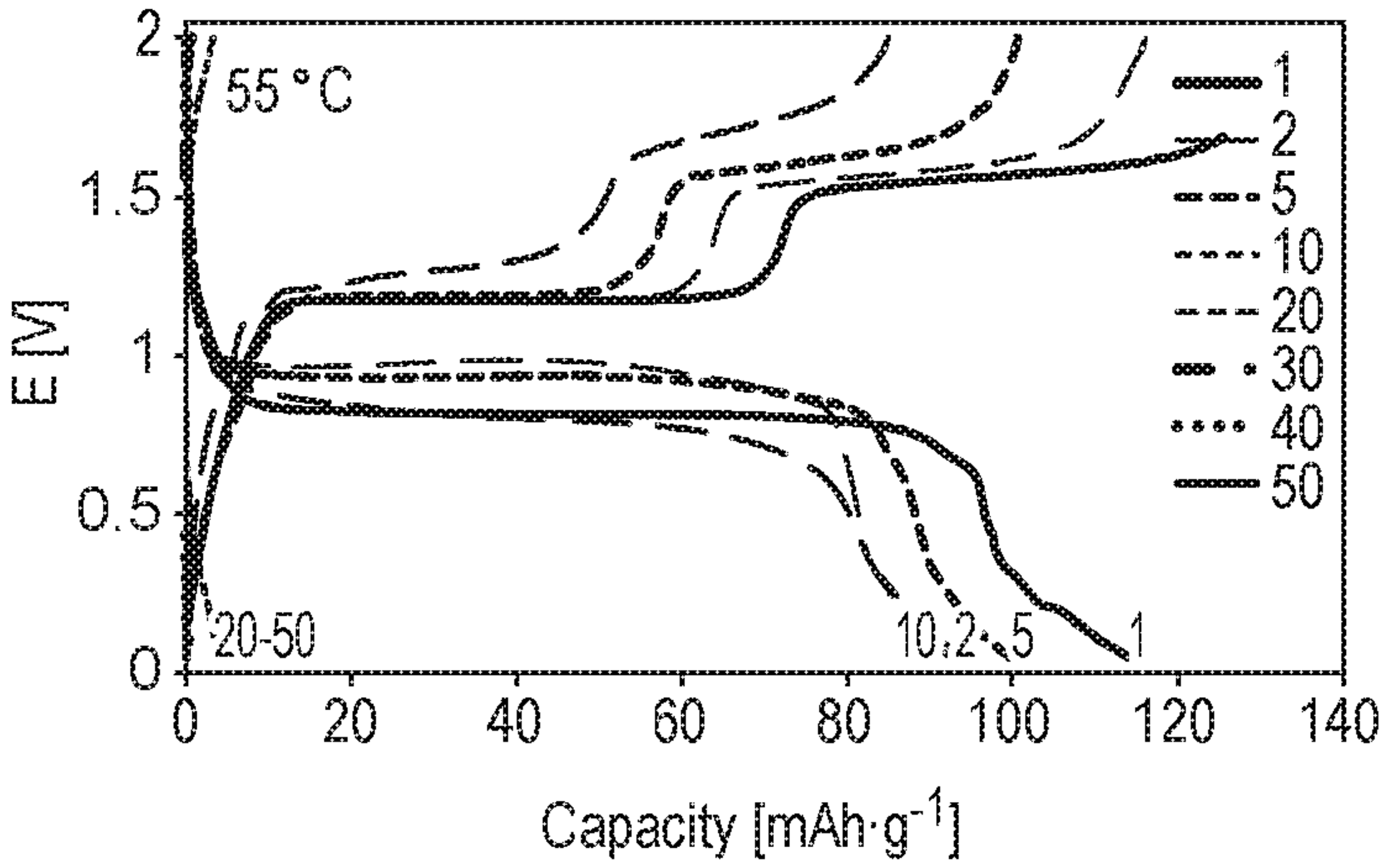

55 °C
E [V]
Capacity [mAh·g^{-1}]
0
0.5
1
1.5
2
0
20
40
60
80
100
120
140
1
2
5
10
20
30
40
50
20-50
10
2
5
1

FIG. 13

MAGNESIUM SALTS

The present invention relates to salts of magnesium. Additionally, the present invention relates the use of the magnesium salts as electrolytes in a cell or battery.

The drive to increase power densities of rechargeable batteries past those currently accessible in established lithium-ion cells for portable electronics has brought about increased interest in developing multivalent battery systems with superior theoretical energy densities. In particular, considerable research focus has been placed on magnesium-ion cells owing to the high theoretical volumetric energy density of magnesium metal anodes as well as potential safety, cost, and environmental benefits. Lithium-ion cells can also form Li dendrites, which have been found to cause short circuiting and dangerous thermal runaway. Magnesium does not readily form dendrites over multiple charge cycles. Furthermore, magnesium is highly earth-abundant and has a lower costs of production than lithium, and magnesium metal can be used directly as an anode material.

Despite being an attractive alternative to lithium-ion technology, development of magnesium-ion systems continues to be limited by a lack of electrolyte systems that are stable at both the magnesium anode and cathode materials that operate at potentials greater than 3.5 V. Many established magnesium-ion electrolyte systems gradually decompose at the electrode surfaces and result in magnesium-impermeable layers that passivate the electrodes. Additionally, many high-voltage electrolytes (stable to at least 3.4 V) are chloride-containing and are thought to result in the corrosion of common battery components such as stainless steel. Accordingly, new directions in magnesium-ion electrolyte development have focused on the synthesis and use of chloride-free salts.

It has been recognised theoretically that alkaline earth metals such as magnesium could be used as electrolyte solutions in electrochemical cells and batteries. Magnesium is both highly abundant in the Earth's crust and therefore less expensive per ton than other Alkali and Alkaline Earth metals. In addition, magnesium has a higher charge capacity than lithium. Furthermore, in a magnesium-ion cell, magnesium metal can be used as the metal anode without the risk of thermal runaway due to dendrites not forming on the magnesium metal. However, despite this knowledge magnesium has not been widely adopted as an electrolyte or as a material for anodes because of difficulties in forming electrolytes that are easy to handle and manufacture, stable over a wide voltage range, and also compatible with multiple electrodes.

In a first aspect, the present invention provides a salt of the formula:

$$Mg[Al(R)_4]_2$$

wherein R represents a halogen-free compound selected from a deprotonated alcohol or thiol; or an amine; or a mixture thereof.

The general formula of the present invention defines a set of magnesium aluminate salts which can be made from a common precursor ($Mg(AlH_4)_2$ without requiring strongly electron withdrawing functional groups on the deprotonated alcohol, thiol or amine, for example halogens. However, the salt could be described more broadly as comprising a deprotonated alcohol, thiol or amine R group which are free of any strongly electron withdrawing groups. Such alcohols, thiols or amines are more readily available and easier to handle for synthesis. Thus, large scale manufacture of the salt of the present invention can be more cost effective and simpler than manufacturing of magnesium aluminate salts of the prior art.

The halogen-free alcohol, thiol or amine is aromatic. Phenoxy groups, or aromatic thiols or amines can provide a salt with improved coordination stability when not provided with halogen groups. In addition, the sterics around the coordination centres (i.e. magnesium and aluminium) can be improved in contrast to using sterically hindered alkyl groups. Specifically, the organic moiety of the halogen-free alcohol, thiol or amine may be based on; iso-propyl, tert-butyl or phenyl. More specifically, R may represent only one halogen-free deprotonated alcohol, for instance phenol, iso-propanol or tert-butanol.

The salt may be crystallised in an organic solvent. The solvated salt gives rise to an electrolyte with improved oxidative stability and good electrochemical performance. Preferably the organic is chloride-free, as chloride-containing solvents are thought to result in the corrosion of common battery components such as stainless steel. Specifically, the organic solvent may be dry DME, 2-methyl-THF, diglyme, triglyme, tetraglyme or THF, since both can improve the electrochemical performance of the resulting electrolyte.

In a second aspect, the present invention provides an electrolyte comprising a salt in accordance with the above Formula (i). The electrolyte may comprise the salt as an additive to a conventional electrolyte, or the salt may be used in a pure solution to form, with an appropriate solvent, an electrolyte by itself. The electrolyte may further comprise an $Mg(PF_6)_2$ additive.

In a third aspect, the present invention provides a cell or battery comprising an electrolyte in accordance with the above Formula (i). The salts of the present invention do not suffer from some of the same disadvantages observed with the use of lithium salts in electrochemical cells or batteries. In addition, the salts of the present invention can be used in electrolytes in a number of cell or battery systems. More specifically, the cell or battery can be, for example, a lithium cell or a lithium-ion cell. However, the cell or battery using the salts of the present invention may be more generally described as a metal based, or a metal-ion based cell or battery. Examples of other metal or metal-ion based cells or batteries may include magnesium, calcium or aluminium metals or ions. When using the salt of the present invention in an electrolyte in metal cell or battery, metals such as magnesium, calcium or aluminum may be used as the metal anode without the risk of the salt decomposing.

In order that the present invention may be more readily understood, an embodiment of the invention will now be described, by way of example, with reference to the accompanying Figures, in which:

Figure 1 is an X-ray single crystal structure of a salt of the present invention;

Figure 2 is an X-ray single crystal structure of a salt of the present invention;

Figure 3 is a ^{1}H NMR spectrum of magnesium tertbutoxyaluminate (1);

Figure 4 is a ^{13}C NMR spectrum of magnesium tertbutoxyaluminate (1);

Figure 5 is a ^{27}Al NMR spectrum of magnesium tertbutoxyaluminate (1);

Figure 6 is a ^{1}H NMR spectrum of magnesium phenoxyaluminate (2);

Figure 7 is a ^{13}C NMR spectrum of magnesium phenoxyaluminate (2);

Figure 8 is a ^{27}Al NMR spectrum of magnesium phenoxyaluminate (2);

Figure 9 shows LSV measurements of an electrolyte solution of magnesium tertbutoxyaluminate (1) in THF;

Figure 10 shows LSV measurements of an electrolyte solution of magnesium phenoxyaluminate (2) in DME ;

Figure 11 shows CV measurements of an electrolyte solution of magnesium phenoxyaluminate (2) in DME using a Pt working electrode;

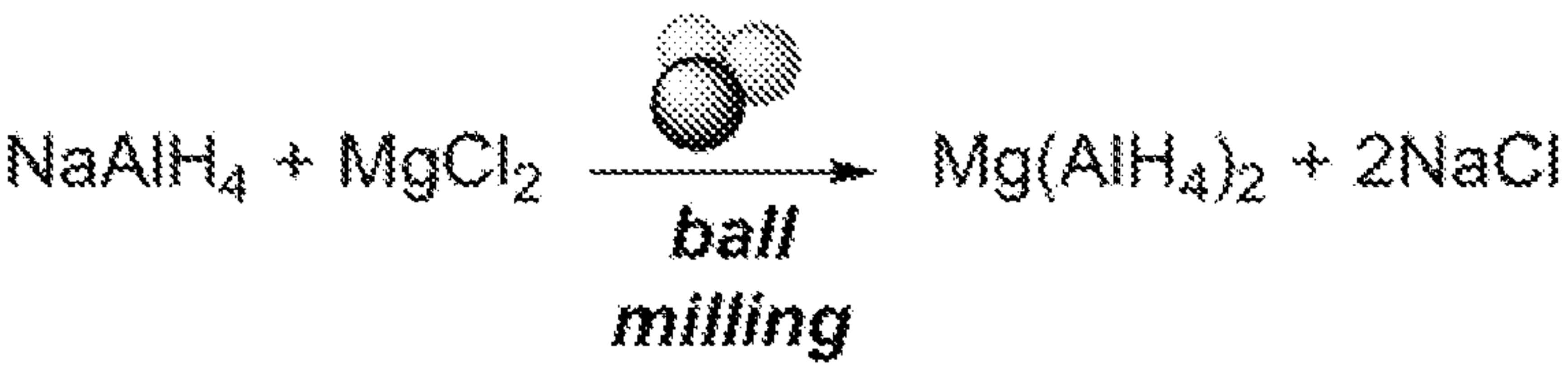
Figure 12 shows the cycling behaviour of an electrolyte solution of magnesium phenoxyaluminate (2) in DME in a coin cell constructed using a magnesium ribbon anode and a Chevrel phase cathode, cycling at room temperature; and

Figure 13 shows the cycling behaviour of an electrolyte solution of magnesium phenoxyaluminate (2) in DME in a coin cell constructed using a magnesium ribbon anode and a Chevrel phase cathode, cycling at 55 °C.

The present invention will now be illustrated with reference to the following examples.

Example 1 – Synthesis of $Mg(AlH_4)_2$ Precursor

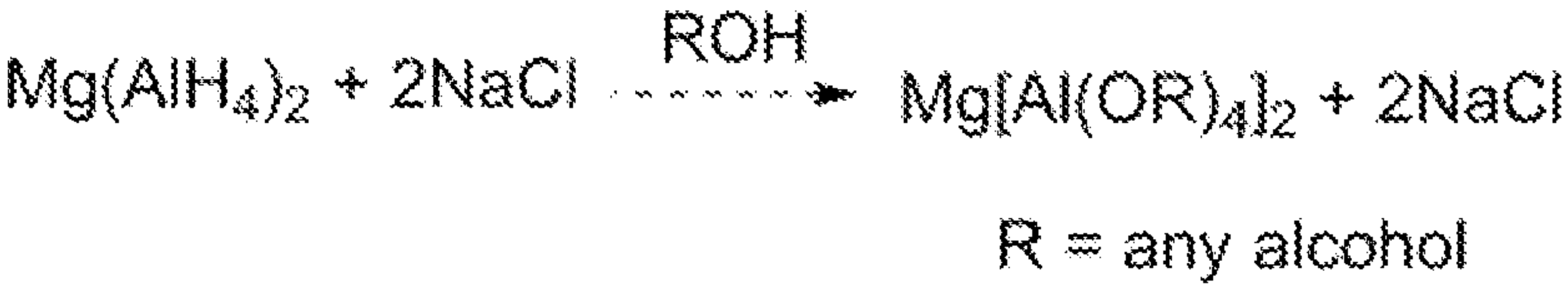
A mixture of sodium aluminium hydride from XXX and magnesium chloride from XXX in a ratio of 2:1 was ball-milled for an hour to produce a mixture of magnesium aluminium hydride and sodium chloride at a theoretical 42.5 wt% of magnesium aluminium chloride (scheme below).



The resulting magnesium aluminium hydride mixture offers a general platform for the synthesis of magnesium aluminates, as will be shown by the following examples.

Example 2 – Synthesis of Magnesium Aluminates Using Alcohol

Magnesium aluminates were synthesized by treating magnesium aluminium hydride with various fluorinated/non-fluorinated alkyl and aryl alcohols in dry THF or DME (Scheme below).



$$Mg(AlH_4)_2 + 2NaCl \xrightarrow{ROH} Mg[Al(OR)_4]_2 + 2NaCl$$

R = any alcohol

These reactions were followed by filtration under inert atmosphere to remove insoluble impurities (i.e. sodium chloride and aluminium-containing by-products). The resulting magnesium aluminates were retrieved, typically as THF or DME solvates, in moderate to high yields (77–94%). The particular alcohols that were used in the synthesis were (1) tert-butanol; and (2) phenol.

Example 3 – Characterisation of Magnesium Aluminates

A single crystal was obtained from THF containing magnesium tertbutoxyaluminate (1), and magnesium phenoxyaluminate (2), as shown in Figures 1 and 2, respectively. X-ray analysis was carried out on data collected with a Bruker D8-Quest PHOTON-100 diffractometer equipped with an Incoatec IμS Cu microsource (λ = 1.5418 Å). and confirmed the complex to be the desired salt.

Multinuclear NMR spectra of the powder of the two magnesium aluminates is shown in Figures 3 to 8. Magnesium tertbutoxyaluminate (1) exhibits the following NMR signals: ^{1}H NMR (C_6D_6) δ 1.48 (s, 1H), 1.46 (s, 1H) ppm; ^{13}C NMR (C_6D_6) δ 71.82, 68.62, 34.20, 33.24 ppm; ^{27}Al NMR (DME) δ 49.17 ppm. Magnesium phenoxyaluminate (2) exhibits the following NMR signals: ^{1}H NMR (C_6D_6) δ 7.08 – 6.99 (m, 32H), 6.76 (t, J = 7.2 Hz, 8H), 3.64 (s, THF), 1.27 (s, THF) ppm; ^{13}C NMR (C_6D_6) δ 156.89, 129.99, 121.16, 120.44, 69.99, 25.11 ppm; ^{27}Al NMR (DME). NMR spectra were recorded at 298.0 K on a Bruker 400 MHz AVIII HD Smart Probe spectrometer (^{1}H at 400 MHz, ^{13}C 101 MHz, ^{27}Al 104 MHz) unless otherwise specified. Chemical shifts (δ, ppm) are given relative to residual solvent signals for ^{1}H and ^{13}C and to external $Al(NO_3)_3$ for ^{27}Al.

Example 3 – Use of Magnesium Aluminates as an Electrolyte Salt

All cyclic voltammetry (CV) and linear sweep voltammetry (LSV) experiments reported below were performed in a glovebox (MBraun) under an atmosphere of dry argon using dry solvents. Cyclic voltammetry and linear sweep voltammetry were performed using an IVIUM CompactStat.

A solution of the magnesium aluminates above (1) and (2) in dry organic solvent was prepared at a concentration of 0.25 M. A solution of magnesium tert-butoxyaluminate (1) in THF was found to exhibit poor oxidative stability on stainless steel (ss-316), aluminium, copper, gold, and platinum electrodes, with the onset of oxidation occurring at around 1 V vs magnesium on each electrode, as shown in Figure 9.

In contrast to magnesium tertbutoxyaluminate (1), a solution of magnesium phenoxyaluminate (2) in DME exhibits moderate oxidative stability with the electrodes that were tested, showing onsets of oxidation between 1.5 V (aluminium, gold and platinum) and 2.2 V ss-316 vs magnesium, as shown in Figure 10. A minor anodic process beginning around 1 V vs magnesium is observed on copper, followed by a larger process at approximately 2.3 V vs magnesium.

CV was used to examine the ability of these 0.25 M magnesium aluminate solutions to facilitate magnesium plating and stripping using a platinum working electrode.

CV measurements of magnesium aluminate (1) in THF did not show evidence of magnesium plating/stripping behaviour between -0.5 V and 1 V vs Mg.

CV of magnesium aluminate (2) in DME shows clear plating and stripping behaviour on platinum between -0.5 V and 1 V vs magnesium over 50 voltammetric cycles, as shown in Figure 11. Plating overpotentials are observed to decrease from -0.41 V to -0.29 V vs magnesium over the 50 cycles.

The electrochemical behaviour of 0.25 M DME solutions of magnesium aluminate (2) was further examined in magnesium full cells constructed using Chevrel phase (Mo6S8) cathodes, magnesium ribbon anodes, and stainless steel current collectors both at room temperature and 55 °C.

Generally, the magnesium aluminate electrolytes exhibited better reversibility, maintained higher capacities over more charge-discharge cycles, and could be cycled at higher rates at 55 °C than at room temperature, as shown in Figures 12 and 13. At room temperature, full cells containing magnesium aluminate (2) typically reached a maximum gravimetric capacity of around 80 mAh·g-1 (Figure 12). However, at 55 °C, full cells containing the same electrolytes maintained gravimetric capacities at around 100 mAh·g-1 over 10 charge-discharge cycles with small to moderate overpotentials (Figure 13).

Claims

1. A salt of the formula:

$$Mg[Al(R)_4]_2$$

R represents a halogen-free compound selected from a deprotonated alcohol or thiol; or an amine; or a mixture thereof; and .

wherein one of the halogen-free alcohol, thiol or amine is aromatic.

2. The salt in accordance with Claim 1, wherein one of the organic moiety of the halogen-free alcohol, thiol or amine is based on; tert-butyl or phenyl.

3. The salt in accordance with any one of the previous claims, wherein R represents a halogen-free deprotonated alcohol.

4. An electrolyte comprising a salt in accordance with any one of Claims 1 to 3.

5. The electrolyte in accordance with Claim 4, wherein the electrolyte further comprises an $Mg(PF_6)_2$ additive.

6. A cell or battery comprising an electrolyte in accordance with any one of Claims 4 or 5.

7. The cell or battery according to Claim 6, wherein the cell or battery is a magnesium cell or battery or a magnesium-ion cell or battery.