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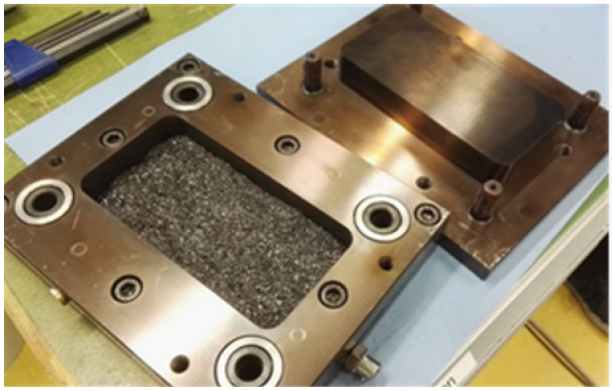
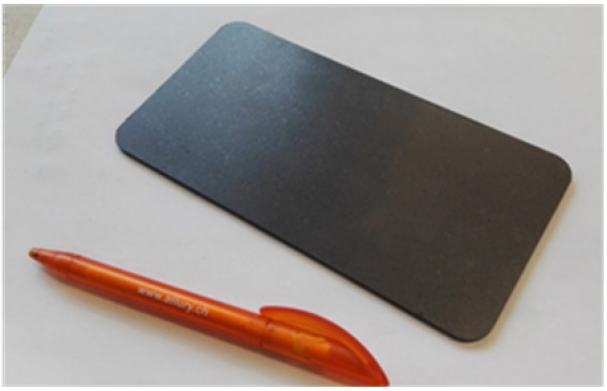
Transport, Energy and Communication DETEC

Swiss Federal Office of Energy SFOE
Energy Research

Final report

Advanced polymer composites for thin bipolar plates for proton exchange membrane fuel cells (CompBiPol)





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Summary

In the near future most engines will be powered electrically by batteries or by fuel cells. One of the major factors limiting fuel cell commercialization is the development of bipolar plates. Their characteristic requirements are a challenge for any class of material, and none meets yet these requirements exactly. This project focused on the development of innovative polymer based composites suitable for bipolar plates. The developed composites needed to fulfil the given requirements concerning electrical and thermal conductivity and mechanical properties and additionally ensure the route towards industrial production. Various potentially suitable electrically conductive fillers, such as graphite, carbon black, carbon fibres, carbon nanotubes, and graphene, and thermoplastic, such as Polypropylene (PP), Polyamide 12 (PA12) and Liquid Crystal Polymer (LCP) as well as thermoset, such as epoxy resin (EP), polymers were used as matrices. The samples were tested with regard of their through-thickness electrical conductivity and flexural properties. The effect of plate thickness, matrix material and filler composition was systematically investigated. It was also found out the surface preparation of the samples and the applied pressure during the electrical resistance measurements have as significant effect on the measured electrical conductivity. Among the compounds tested, polypropylene (PP) based samples showed the best processability via compression moulding and resulted in the best electrical properties. A maximum electrical conductivity of 46 S/cm (target value: 50 S/cm) was achieved, using a multi-filler approach with carbon based fillers of different form and size. These results meet or even exceed those found in the literature and it is strongly believed that optimization of the manufacturing process can push the electrical conductivity value above the target of 50 S/cm.

Zusammenfassung

In naher Zukunft werden die meisten Motoren elektrisch oder mit Brennstoffzellen betrieben werden. Einer der Hauptfaktoren, der die Kommerzialisierung von Brennstoffzellen einschränkt, ist die Entwicklung von Bipolarplatten. Ihre charakteristischen Anforderungen stellen eine Herausforderung für jede Materialklasse dar, und keines erfüllt diese Anforderungen genau. Dieses Projekt konzentrierte sich auf die Entwicklung innovativer polymerbasierter Komposite, die für Bipolarplatten geeignet sind. Die entwickelten Verbundwerkstoffe müssen die gestellten Anforderungen hinsichtlich elektrischer und thermischer Leitfähigkeit und mechanischer Eigenschaften erfüllen und zusätzlich den Weg zur industriellen Produktion gewährleisten. Verschiedene potentiell geeignete elektrisch leitfähige Füllstoffe, wie Graphit, Ruß, Kohlenstofffasern, Carbon Nanotubes und Graphen, und thermoplastische Polymeren, wie Polypropylen (PP), Polyamid 12 (PA12) und Flüssigkristallpolymer (LCP) sowie Duroplaste, wie Epoxidharz (EP) wurden als Polymermatrix verwendet. Die Proben wurden auf ihre elektrische Leitfähigkeit und ihre Biegeeigenschaften hin untersucht. Die Wirkung von Plattendicke, Matrixmaterial und Füllstoffzusammensetzung wurde systematisch untersucht. Es wurde auch herausgefunden, dass die Oberflächenvorbereitung der Proben und der angewendete Druck während der elektrischen Widerstandsmessungen einen signifikanten Einfluss auf die gemessene elektrische Leitfähigkeit haben. Unter den getesteten Verbindungen zeigten Proben auf Polypropylen (PP) -Basis die beste Verarbeitbarkeit durch Formpressen und resultierten in den besten elektrischen Eigenschaften. Es wurde eine maximale elektrische Leitfähigkeit von 46 S/cm (Zielwert: 50 S/cm) erreicht, wobei ein Multi-Füllstoff-Ansatz mit kohlenstoffbasierten Füllstoffen unterschiedlicher Form und Größe verwendet wurde. Diese Ergebnisse erfüllen oder übertreffen sogar diejenigen, die in der Literatur gefunden wurden, und es wird stark angenommen, dass durch eine Optimierung des Herstellungsverfahrens der Wert der elektrischen Leitfähigkeit von 50 S/cm erreicht werden kann.

Résumé

Dans un proche avenir, la plupart des moteurs seront alimentés électriquement par des batteries ou par des piles à combustible. Le développement des plaques bipolaires est l'un des principaux facteurs limitant la commercialisation des piles à combustible. Leurs exigences caractéristiques représentent un défi pour toutes les classes de matériaux et aucune ne répond encore à ces exigences avec précision. Ce projet était axé sur le développement de composites innovants à base de polymères adaptés aux plaques bipolaires. Les composites développés devaient répondre aux exigences données en matière de conductivité électrique et thermique et de propriétés mécaniques, tout en garantissant le passage à la production industrielle. Diverses charges électriquement conductrices potentiellement appropriées, telles que le graphite, le noir de carbone, les fibres de carbone, les nanotubes de carbone et le graphène, ainsi que les matériaux thermoplastiques, tels que le polypropylène (PP), le polyamide 12 (PA12) et le polymère à cristaux liquides (LCP) ainsi que les polymers-thermodurcissables, comme la résine époxy (EP), des polymères ont été utilisés comme matrices. Les échantillons ont été testés en ce qui concerne leur conductivité électrique à travers l'épaisseur et leurs propriétés en flexion. L'effet de l'épaisseur de la plaque, du matériau de la matrice et de la composition de la charge a été systématiquement étudié. Il a également été découvert que la préparation de la surface des échantillons et la pression appliquée pendant les mesures de résistance électrique avaient un effet significatif sur la conductivité électrique mesurée. Parmi les composés testés, les échantillons à base de polypropylène (PP) ont montré la meilleure aptitude au traitement par moulage par compression et ont donné les meilleures propriétés électriques. Une conductivité électrique maximale de 46 S/cm (valeur cible: 50 S/cm) a été atteinte en utilisant une approche à charges multiples avec des charges à base de carbone de forme et de taille différentes. Ces résultats atteignent, voire dépassent, ceux que l'on trouve dans la littérature et il est fortement convaincu que l'optimisation du processus de fabrication peut permettre de dépasser l'objectif de la valeur de la conductivité électrique de 50 S/cm.

Contents

List of abbreviations

BMC	Bulk moulding compound
BPP	Bipolar plate
CB	Carbon black
CF	Carbon fibers
CNT	Carbon nanotubes
EG	Expanded graphite
EP	Epoxy resin
FHNW	Fachhochschule Nordwestschweiz
GDL	Gas diffusion layer
GN	Graphene
Gr	Graphite
IKT	Institut für Kunsstofftechnik
LCP	Liequid crystal polymer
MWCNT	Multi-walled carbon nanotube
NG	Natural graphite
PA12	Polyamide 12
PC	Polycarbonate
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cells
PF	Phenol formaldehyde
PMMA	Poly(methyl methacrylate)
POM	Polyoxymethylene
PP	Polypropylene
PPS	Polyphenylene sulphide
PSI	Paul Scherrer Institut
PTFE	Polytetrafluorethylen
SFOE	Swiss Federal Office of Energy
SG	Synthetic graphite
TCA	Titanate coupling agent
US-DoE	United States – Department of Energy
VE	Vinylester

1 Introduction

Bipolar plates are a significant factor in determining the gravimetric and volumetric power density of a fuel cell, typically accounting for more than 80% of the weight of a stack and nearly 2/3 of the volume.

At the same time, the price of the raw material and the often complex processing that goes into manufacturing bipolar plates (BPPs) makes them one of the most expensive parts of the fuel cell. For component developers, the challenge is therefore to reduce the weight, size and cost of the bipolar plate while maintaining the desired properties for high-performance operation [1].

2 Context

2.1 Background / State of the art

The required properties for the BPPs have been reported in the literature according to the United States – Department of Energy (US-DoE) [4]. Furthermore Gloaguen [5] has reviewed these values in his PhD thesis. The suggested properties and values are summarized in Table 1. For this project, the electrical conductivity in the Z direction (through-thickness conductivity) has been selected as a critical property and used for the screening of the various materials. Therefore, all the results of electrical conductivity presented in the following paragraphs are based on through-thickness measurements. Moreover, the flexural properties, the corrosion resistance and the in-plane thermal conductivity of the most promising formulations were characterized.

Properties	**Unit**		**Gloaguen**	**US-DoE**
Electrical Conductivity	S/cm	Z	50	> 100
		XY	100	
Areal specific resistance	Ωcm^2			0.01
Thermal Conductivity	$W.m^{-1}K^{-1}$	Z	20	> 10
		XY	50	
Tensile Properties	MPa	Strength	30	> 41
	GPa	Modulus	10	
Flexural Properties	MPa	Strength	49	> 25
	GPa	Modulus	10	
Compressive Properties	MPa	Strength	70	> 50
	GPa	Modulus	4	
Gas Permeability	$cm^3.s^{-1}.cm^{-2}$			$< 2.10^{-6}$
Corrosion Resistance	$\mu A.cm^{-2}$			< 1

Table 1: Proposed properties and their target values for BPPs according to US-DoE and Gloaguen [5].

2.1.1 Commercial available bipolar plates

A summary of the main BPP materials developers is provided in Figure 1[1]. Their properties are summarized in Table 2.

BPP have traditionally been made from graphitic carbon. Such materials, available for example from POCO Graphite (Texas, USA), offer high electronic and thermal conductivities, low contact resistance, good corrosion resistance and ease of machining. Although still used in some state-of-the-art stacks

and for prototyping flow-field designs, standard graphite plates are being superseded by various metallic and carbon composites – materials that are more robust, thinner and less expensive to manufacture.

On the other hand, flexible graphite is now being used extensively. For example, GRAFCELL from GraphTech (Ohio, US) is a flexible graphite BPP found in fuel-cell vehicles. Flexible graphite is made by “expanding” natural graphite with the help of an intercalating agent and heat treatment – a process that increases the spacing between the planes of the graphite structure by as much as 80 times. The expanded form is then compressed to the desired density and pressed to form the bipolar plate. Flexible graphite meets basic cost targets and has the advantage of very low contact resistance and density (typically 1g/cm^3). It also has excellent sealing characteristics. The downside is that it is mechanically weaker than other BPP materials and has a relatively high gas permeability.

Carbon–polymer composites are made by incorporating carbonaceous material into a polymer binder, thereby producing a material that can be formed by injection or compression moulding. These plates are low-cost, lightweight and amenable to rapid processing since the flow-field geometry can be moulded directly into the composite. However, the performance of carbon–polymer composites has, until recently, tended to be inferior to that of other materials – largely a result of their low electrical conductivity. In plane electrical conductivity has increased from as little as 2.4 S/cm for carbon-black and polyvinylidene-fluoride (PVDF) composites to over 300 S/cm for composites with graphite loadings as high as 93% (reported by the Gas Technology Institute, for example). SGL Technologies (Germany) offers different types of composite bipolar plates under the tradename Sigracet (Table 2). Sigracet PPG86 is a PP based compound which follows a three step process. The graphite filler, the PP binder and possible additives are compounded and granulated in a twin screw extruder. The granules can be fed into an IM machine. BPPs are then injection moulded. Finally, the polymer rich skin is broken by abrasive blasting. The Sigracet BB4 has to be conditioned after compounding, and post-cured after the abrasive blasting.

Another overview of commercial composites for bipolar plates is given in Table 3 [3].

Bac2 (UK) has introduced ElectroPhen as an electrically conductive polymer whose polymerisation generates nano-structures of conductive pathways locked within the polymer chains. Patents have been filed on the material. A 80% graphite filler content in the form of large particle site flake or shaped granules is typically used [6]. The properties of these bipolar plates are shown in Figure 2.

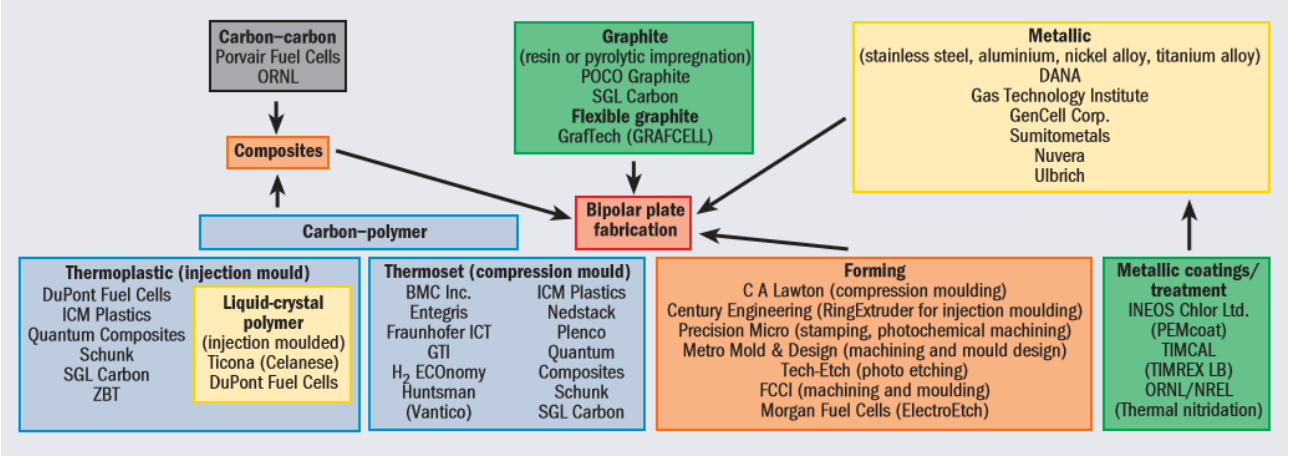

Figure 1: Main bipolar-plate materials developers – Status 2005 [1].

Source	Bulk Moulding Compounds Inc. (BMC 940)	SGL Carbon SIGRACET (BBP 4)	SGL Carbon SIGRACET (PPG 86)	Porvair Fuel Cells	POCO Graphite (AXF 5Q) (unimpregnated)	SS316L
Type	**Thermoset**	**Thermoset**	**Thermoplastic**	**Carbon–carbon composite**	**Graphite**	**Metallic**
Density (g/cm^3)	1.82	1.97	1.84	1.2–1.3	1.78 (20% porous)	8
Electronic conductivity (S/cm)	100* 50†	200* 41.6†	55.6* 18.2†	>500*	680.3	13513
Coefficient of thermal expansion $\times 10^{-6}$ (K^{-1})	30	5.8	49	2	7.9	16
Thermal conductivity (W/m K)	18.5† (at 85 °C)	20.8	14	>35*	95	16.3
Flexural strength (kg/cm^2)	407.8	407.8	358.6	420–500	878.8	
Permeability coefficient (10^{-5} cm^3/cm^2 s)		2.5	3.5	<0.2		Gas tight
Max operating temperature (°C)	200 glass transition	≤180	≤80	>400	>400 (pyrolytic impregnation) 150 (resin impregnation)	1400 m.p.

* In-plane property † Through-plane property

Table 2: Properties of commercial available bipolar plates [1].

Source	Polymer	Graphite/glass or carbon reinforcing fiber (wt/wt%)	Conductivity/S cm^{-1}		Mechanical strength/MPa	
			In-plane	Through-plane	Tensile	Flexural
Target			>100[a]	—	41.0[b]	59.0[b]
LANL[12]	Vinyl Ester	68/0	60	—	23.4	29.6
GE[3]	PVDF	64/16 CF	109	—	—	42.7
Virginia Tech[8]	PET	65/7 GF	230	18–25	36.5	53.0
Virginia Tech	PPS	70/6 CF	271	19	57.5	95.8
Virginia Tech[14]	PPS core PVDF skin	70/6 CF core 80/0 laminate	147–350	14–32	34.4	48.9

[a] DOE target for conductivity.[15] [b] Plug Power targets for mechanical strength.[7]

Table 3: Comparison of electrical and mechanical properties for polymer composite material used for the production of bipolar plates [3].

Property	Value	Units
Density	1.79	g/cm^3
Flexural strength	32	MPa
Shore "D" Hardness	71	
In-plane electrical conductivity	130	S/cm
Through-plane conductivity	40*	S/cm
Surface resistance	0.254	mΩ
Thermal Conductivity	44	W/mK
Temperature stability	180	°C

The absolute performance of this material is dependent on the form factor of the component moulded. The above results were achieved using a selection of moulded test pieces.
*Based on 3mm thickness and includes surface resistance

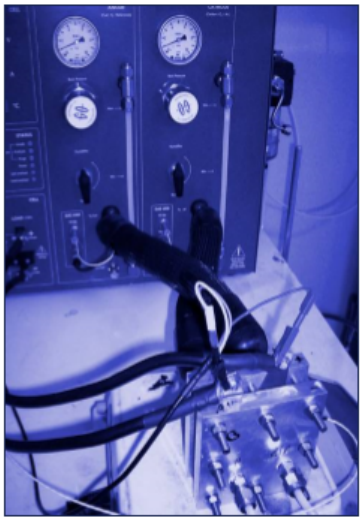

Figure 2: EP1109 for LTPEM & DMFC Bipolar Plates from Bac2.

2.1.2 Literature on composites for bipolar plates

A number of reviews on composite materials for bipolar plates can be found in the literature [2, 7-10].

2.1.2.1. Polymers

In principle, there are two types of polymers that can be used in composite bipolar plates; thermosets and thermoplastics.

Thermosets such as vinylesters, epoxy and phenolic resins have been widely investigated as matrices for composite bipolar plates. Their low viscosity and high temperature and chemical resistance count to their advantages. Sometimes it is necessary to conduct a post-cure reaction to eliminate residual monomers that could poison the membrane electrode assembly of the PEM fuel cell, decreasing their ionic conductivity.

For the thermoplastics, their melting temperature, Tm, is an important property for defying their processing parameters and also service temperature. Some references for low temperature thermoplastics such as PP and PET can be found in the literature [11, 12] while high-temperature thermoplastics such as PPS and PES have already tested for bipolar applications reaching most of the desired requirements [13, 14]. An advantage of thermoplastic polymers is their possibility of fast processing and recycling in contrast to thermosets.

Semi crystalline thermoplastic polymers are identified as being preferable as a matrix for high temperature bipolar plates due to their sharp Tm and low melt viscosities that enable good dispersion of carbon fillers. PPS was found to be most suitable due to its higher chemical stability and higher heat deflection temperature. Liquid crystal polymers (LCP) have been also identified as good matrices for composite bipolar plates [15].

Furthermore, intrinsically conductive polymers (ICPs) such as polyanilines (PANI), polypyrroles and polyphenylenes have been used as part of conductive composites due their high conductivity. They have been used as a mixture with other polymers. However, [11] showed that the additions of PANI to PP/CB/GP composites was unsuitable due to the poor thermal stability of PANI. The company Bac2 is currently the only manufacturer to use a patented electrically conductive polymer called ElectroPhen®.

Wetting of the filler surface by the polymer depends on their surface energies. If the difference between the surface energies of polymer and filler is small, then the filler will be efficiently wetted by the resin. Consequently, more resin will be necessary to coat the filler surface. Then, the concentration of fillers should increase before the particles encounter each other. Thus, the percolation threshold of the composite and its resistivity increase accordingly. Therefore, it is important to use resins that present higher surface energy than the conductive fillers used to manufacture composite bipolar plates in order to minimize this effect [11].

2.1.2.2. Conductive Fillers

The optimization of the electrical conductivity of polymer matrix composite bipolar plates plays a leading role thereby demanding many efforts to the development of increasingly conductive materials. Enhancement of this property is only possible if the percolation threshold of the conductive filler in the polymer matrix is known. However, the percolation threshold is only the tip of the iceberg and there is much more to consider. The intrinsic conductivity of fillers depends on their nature, degree of crystallinity, size and morphology. An overview of the maximal conductivity obtained for different composites filled with one type of carbon fillers is given in Figure 3.

Furthermore, a balance between electrical and mechanical properties is required. An overview of the flexural strength as a function of the in-plane conductivity is shown in Figure 4. A direct way to improve the electrical properties of composites is to increase the carbon filler content. This strategy is however limited by the wetting problem and the loss in flexural strength that accompanies it. Another way consists in optimizing the mix of carbon fillers in the composite. This solution seems to give interesting results since the composites filled with different carbon fillers (Gr-CB, Gr-CF, Gr-CNT, Gr-CB-CF) have better mechanical properties than the others composites filled with one carbon filler (Gr).

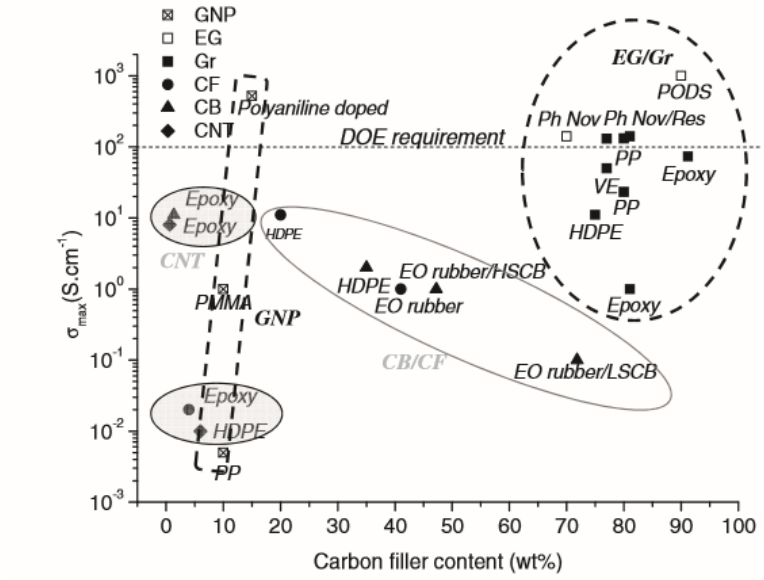

Figure 3: Maximal conductivity σ_{max} obtained for different composites filled with one type of carbon fillers: expanded graphite EG, graphite nanoplatelets GNP, graphite Gr, carbon fiber CF, carbon black CB and carbon nanotube CNT as a function of carbon filler content [2]

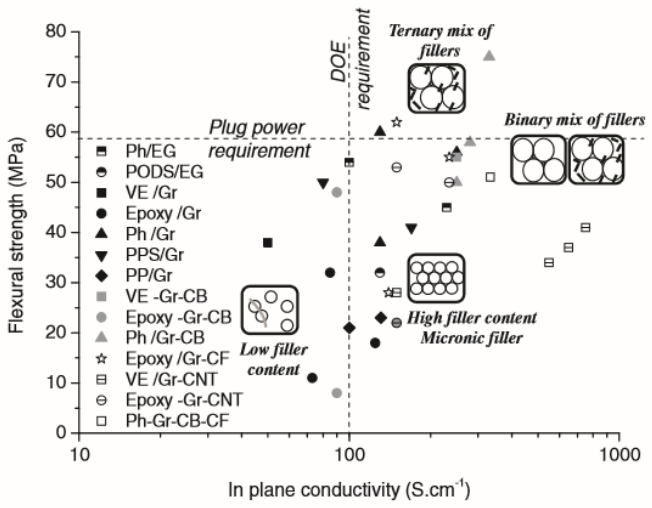

Figure 4: Flexural strength versus in plane conductivity for different composite systems [2].

An overview of the properties of polymer composites for bipolar plates that can be found in the literature is given in Table 4. Few of the studies report the through plane conductivity values which are critical for the specific application. It is hard to compare the values one to one as the conductivity is measured with different configurations and methods and the geometry of the samples varies as well. These parameters have a significant effect on the measurements of the electrical conductivity, as has been verified in this project and reported within the next paragraphs.

Source	Matrix	Fillers	Content%	Manufacturing Method	In-Plane Conductivity (S/cm)	Through-Plane (S/cm)	Flexural Strength (MPa)	Tensile Strength (MPa)
US 4,214,969 [16] GE	Polyviniledene fluoride (PVDF) (eg. Kynar grade 461 obtained from PennWalt Corporation)	GrP (eg. graphite powder (Union Carbide Grade GPI95)	74 wt%	Compression moulding	119		35-37	
US 4,339,322 [17] GE	PVDF	EG/CF	64/16		109			42.7
US 6,248,467 [18] LANL	Vinyl ester (Hetron 922)	Gr and GF, CF, PE or cotton fibers	68 wt%	Compression moulding	60		29.6	23.4
US 6,171,720 [19] ORNL	Phenolic	CF		Conventional slurry moulding techniques	200-300			
[20]	Thermoplastic			Injection moulding		150		
[21]	PET	EG/GF	65/7 wt%	Wet-lay (paper making)/ Compression moulding	230	18-25	36.5	53
[22]	Nylon-6	S316L Stainless Steel Fibers (6.4 mm)	60 wt%	Injection Moulding		Contact resistance 100-260 $m\Omega.cm^2$	52.3	68.5
[15]	LCP	CF/CB	31.7/5.3 vol%	Extruder / Compression moulding	6			
[23]	PET or PPS	EG/CF or GF	70-80/6-9 wt%	Wet-lay composite sheet/ Compression moulding	>250		95.8	57.5
[13]	PPS core and PVDF/G	Gr/CF	70 / 6 wt%	Wet-lay lamination/ Compression moulding	292		37	60
[24]	Novolac-type phenol resin	Flake-like graphite/EG	67.5 / 7.5 wt%	Preforming (mixing; pre-curing) / Compression moulding	251			50
[11]	PP	Synthetic Gr/ CB	20/25 wt%	Melt compounding Compression moulding	35			
[12]	PP	Gr/MWCNT	79.4/0.80 wt%	Melt compounding Compression moulding	548			32
[14]	PPS	Gr	80 wt%	Ball milling/ Hot pressing	119			55.7
[25]	Epon® 826 and Araldite® DY3601, curing agent — DDS	EG/CB	40 – 70 wt% (of which max.5 CB)	Solution intercalation method	100 - 900	79	40-82	25-45

[26]	Novolac phenolic resin	EG	40-50 wt%	Compression molding	110-150		49-54	
[27]	EP	Gr/CB Gr/MWCNT Gr/CF (3 mm)	70/5 vol% 73/2 vol% 68/7 vol%	Mixing / Compression moulding	153.8 254.7 237		20 50 60	
[28]	Vinylester	Gr/ Modified MWCNT/ copper mesh / aluminum mesh	70 wt% 0-2 wt%	BMC	643	37.8 36.7 22.9		
[29]	Novolac type phenol formaldehyde resin	Gr Gr/CB (Vulcan XC72) Gr/CB/CF	65 vol% 65/5 vol% 60/5/5 vol%	Mixing / Compression moulding	120 260 258.5	25 80 91.8		40 46 55.3
[30]	EP	EG	69 wt%	Compression molding	120		45	
[31]	Resol-PF resin	Gr/CB Gr/CB/CF Gr/CB/CF/GN	70/5 65/5/5 64/5/5/1	Mixing / Compression moulding	425 415 435	115.7 99.7 130		46 54 57
[32]	bisphenol-F type EP / phenol novolac hardener	Gr/MWCNT Gr/CF	73/2 vol% 68/7 vol% 70/5 vol%	Mixing / Compression moulding	250 240 160	35 30 15		45 55 18
[33]	Benzoxazine resin (BA-a)	GN	50 wt% 60 wt%	Mixing / Compression moulding	120 350			50 40

Table 4: Overview of the properties of polymer composite for bipolar plates.

2.2 Motivation of the project

GREENGT has filed a patent for a new design of bipolar plates (PCT/IB2015/058773) that can lead to more efficient and lighter fuel cells. This invention requires a suitable composite material for the bipolar plate, i.e. having a good electrical and thermal conductivity, a good tightness for the gas and water, and mechanical properties adapted to thin sheet production. Such bipolar plate is not yet available in the market. In the frame of this project, GREENGT together with FHNW will work towards this goal, by developing innovative composite materials that will fit the requirements of GREENGT's invention.

2.3 Goals

This project focused on the development of innovative polymer based composites suitable for bipolar plates in proton exchange membrane fuel cells. The main application is the high value transport industry. The developed composites must fulfil the given requirements of such an application (Table 1) and additionally ensure the possibility to be formed into thin plates.

3 Approach and methodology

3.1 Materials

The composite materials tested within the frame of this project consisted of a polymer matrix and various conductive fillers mainly based on carbon. A multi-filler approach was followed, as this, according to the literature survey, was expected to facilitate synergistic effects and thus higher levels of electrical properties.

3.1.1 Polymers

The routes of thermoset and thermoplastic polymers as matrix for the BP plates were considered. In the case of thermosets, the following systems were tested.

Provider	Product	Polymer
Huntsman	Araldite LY1564 / Aradur 22962	EP
Huntsman	Araldite LY 3585 / Aradur 3475	EP
RossFisch Composites	Oldopal VE 430-01-TV/ Curox M102	VE
sbhpp	FERS F61F	PF

Table 5: Thermoset resins used in this project.

Epoxy resins showed acceptable processability, while VE, Phenolic and PMMA were tested without success.

For the thermoplastic route, the following materials were investigated. These consist of different thermoplastic polymers in a masterbatch form (that means the polymers are already mixed with fillers).

Provider	Product	Polymer	Filler Content [%]
Nanocyl	Plasticyl PP2001	PP	20% MWCNT
Nanocyl	Plasticyl PA1502	PA12	15% MWCNT
Nanocyl	Plasticyl PC1501	PC	15% MWCNT
Nanocyl	Plasticyl POM1001	POM	10% MWCNT
Hyperion Catalysis	MB7015-00	PPS	15% MWCNT
Celanese	VECTRA A625	LCP	25% Graphite

Table 6: Thermoplastic based masterbatches used in this project.

3.1.2 Fillers

The following fillers were tested (Table 7 - Table 10). Most of them are based on carbon and their selection was based on their form, size and intrinsic properties. The product from TFP (Table 9) was in the form of a thin veil and was used as such. Expanded graphite (EG) from Imerys (BNB-90) was investigated as well, as a possible filler. The particle size d90 of this filler was 85 µm. Moreover, metallic fillers were tested as well as highly conductive references.

Provider	Product	Type	Purity [%C]	Particle Size d50 [µm]
Imerys	Timrex KS75	SG	> 99.9	23
Superior Graphite	Purified Natural Flake Graphite 2922A	NG	> 99.9	45
ProGraphite	Natural High-Conductive Graphite	NG	> 98	70
ProGraphite	Natural Conductive Graphite	NG	> 95	25
ProGraphite	Synthetic Micro Graphite	SG	> 99	14

Table 7: Graphite types used in this project.

Provider	Product	Jod-Absorption [mg/g]	DBPAbsorption [ml/100g]	Bulk Density [g/l]
Imerys	ENSACO 250G	N/A	190	170
Cabot	Vulcan XC72-R	235	192	N/A
H.C. Carbon	MECHANO COND 5VP3	82	102	350
Unipetrol	Chezacarb AC-60	950	380	112

Table 8: Carbon black types used in this project.

Provider	Product	Length	Sizing
SGL	Milled CF – C M80-4/240-UN	80 µm	Unsized
Suter-Composites	SCS-Carbon Kurzschnitt	100 – 350 µm	0.1 – 1 % EP
Suter-Composites	SCS-Carbon Schnitzel	3 mm	1.5% EP
TFP	Optiveil CF-Fliess 10 g/m^2	N/A	N/A

Table 9: Carbon fibers used in this project.

Provider	Product	Ag-Content [wt%]	Particle Size d50 [µm]
Altana (Eckart)	eConduct Aluminium 202000	20	18 µm (granular)
Altana (Eckart)	eConduct Copper 421000	10	40 µm (flake)
Altana (Eckart)	eConduct Glass 205000	50	17 µm (flake)

Table 10: Metallic fillers used in this project.

3.2 Composites Preparation

For the preparation of the thermoset based compounds the following route was followed.

1. The resin and hardener were mixed together to a homogeneous mixture with the mixing machine (Figure 8). A mixing time of 1 minute at 800 rotations per minute were used.
2. All fillers were put into the mixed thermoset-system and were mixed until the entire amount of fillers was impregnated. Also for 1 min at 800 rpm.
3. Onto the bottom of the compression mould was layed a pre-cutted PTFE-film of 1 mm thickness to provide an adhesive effect between the compound and the mould surface (Figure 5).
4. The mixed compound was filled onto the PTFE-film and distributed over the mould surface.
5. A further PTFE-film was placed onto the compound to provide an adhesive effect from the upper mould surface

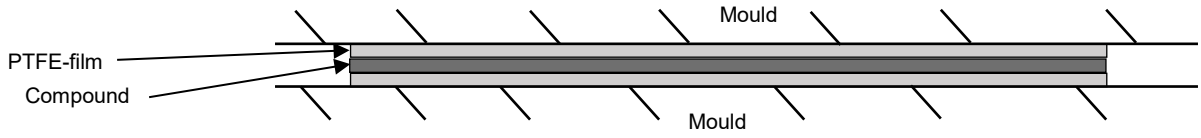

Figure 5: Set up in the mould with PTFE-films

6. The mould was closed and put into the press for 15 minutes at 10 MPa and 130°C (Araldite LY 3585 / Aradur 3475).
7. After cooling the plate was removed. No post-processing was needed.

The hand-compression mould (Figure 6) which was used has a rectangular press area with rounded edges.

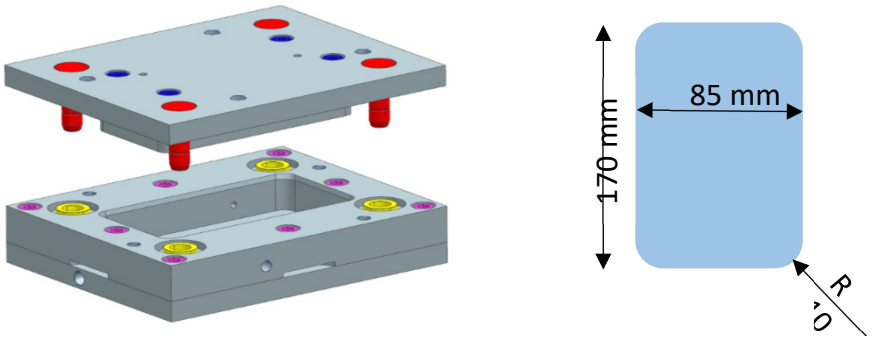

Figure 6: Hand-compression mould as assembly (left) and press area inside (right).

An example for an epoxy based thermoset plate can been seen in Figure 7.

Figure 7: Plate composed of 50% EP, 45% Gr and 5% CB.

Figure 8: Mixing machine (SpeedMixer).

For mixing of the thermoplastics with the different fillers a laboratory kneader (HAAKE Polylab Rheometer) was used (Figure 9). This process was very efficient for the production of highly filled compounds (up to 80% fillers) via the application of temperature and high shearing forces. A mixing time of 10 min and a rotation speed of 60 min^{-1} were used for all compounds, while temperature was varying depending on the polymer matrix (Table 11). The consistency of the compounds after the mixing process was comparable to moistened sand. Different filler compositions resulted in visible differences in texture. The compounds were then grounded in a mortar to powder (Figure 10). By using a sieve, a uniform powder was received and then pressed into plates (Figure 11) via compression moulding (Vogt press).

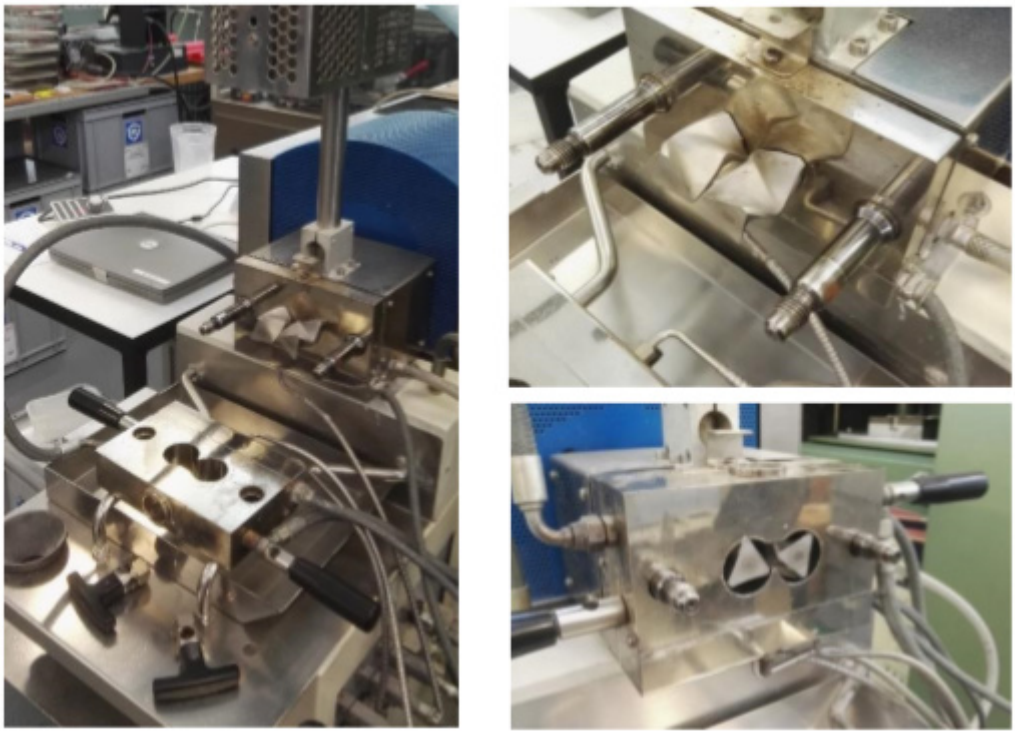

Figure 9: The laboratory kneader (HAAKE Polylab Rheometer).

	PP	POM	PA12	PC	LCP	PPS
Mixing temperature [°C]	180	200	200	240	320	340

Table 11: Mixing temperatures for the various thermoplastics tested in this project.

Figure 10: Preparation of compounds for compression moulding.

Figure 11: Plate in the mould after pressing (left) and demoulded plate (right)

3.3 Characterization

The characterization of the through-thickness conductivity of the different samples took place at the laboratories of Institut für Kunststofftechnik (IKT) of FHNW and also at Paul Scherrer Institut (PSI), for comparison.

At IKT the configuration shown in Figure 12 was used in connection to the digital micrometer MI3250 MicroOhm 10A from METREL.

The electrical conductivity was calculated using a following equation:

$$\sigma = \frac{t}{A \cdot Rtot}$$

Where t and A are the thickness and cross-section area of the samples within the electrodes and R_{tot} the measured resistance. The cross-section area was 6.25 cm^2 while samples of various thickness were tested.

The applied pressure during the measurements had a major effect on the resistance levels. For example when the pressure increases from 1 to 3 MPa the measured resistance drops significantly. Above 3-4 MPa no important various was detected. For this project, the applied pressure was set to 1.6 MPa which is close to the real pressure during the life time of a BPP.

At PSI the configuration shown in Figure 13 was used. Gold coated copper electrodes were also used but the cross-section area was larger (25 cm^2) than that using at IKT and the applied pressure during measuring was 3 MPa. Moreover, flexible and soft graphite films of 0.3 mm thickness were used between the electrodes and the samples for reducing the contact resistance. A constant current of 10 A was applied and the voltage was measured via wires on the surface of the sample (Figure 13 right).

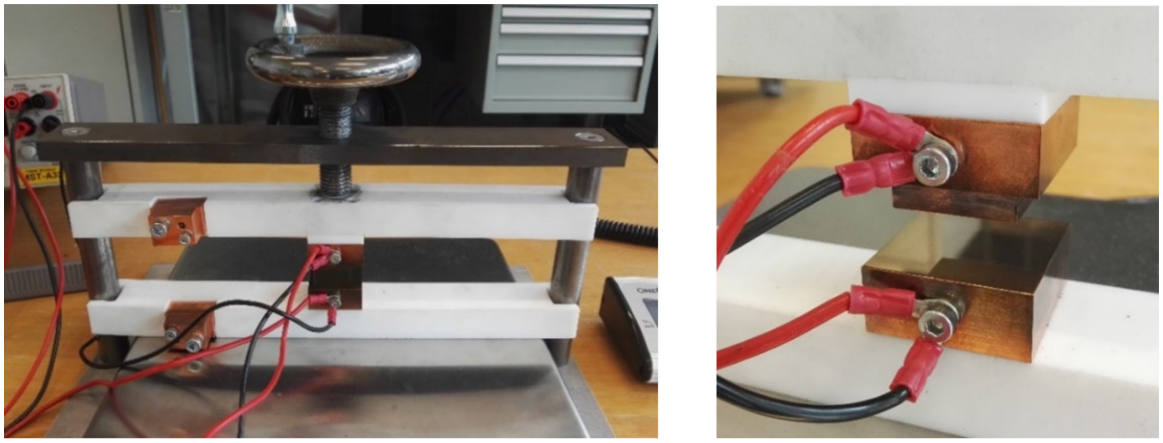

Figure 12: Through-thickness resistance measurements at IKT: Configuration (left) and detail of the gold spattered cooper electrodes used (right).

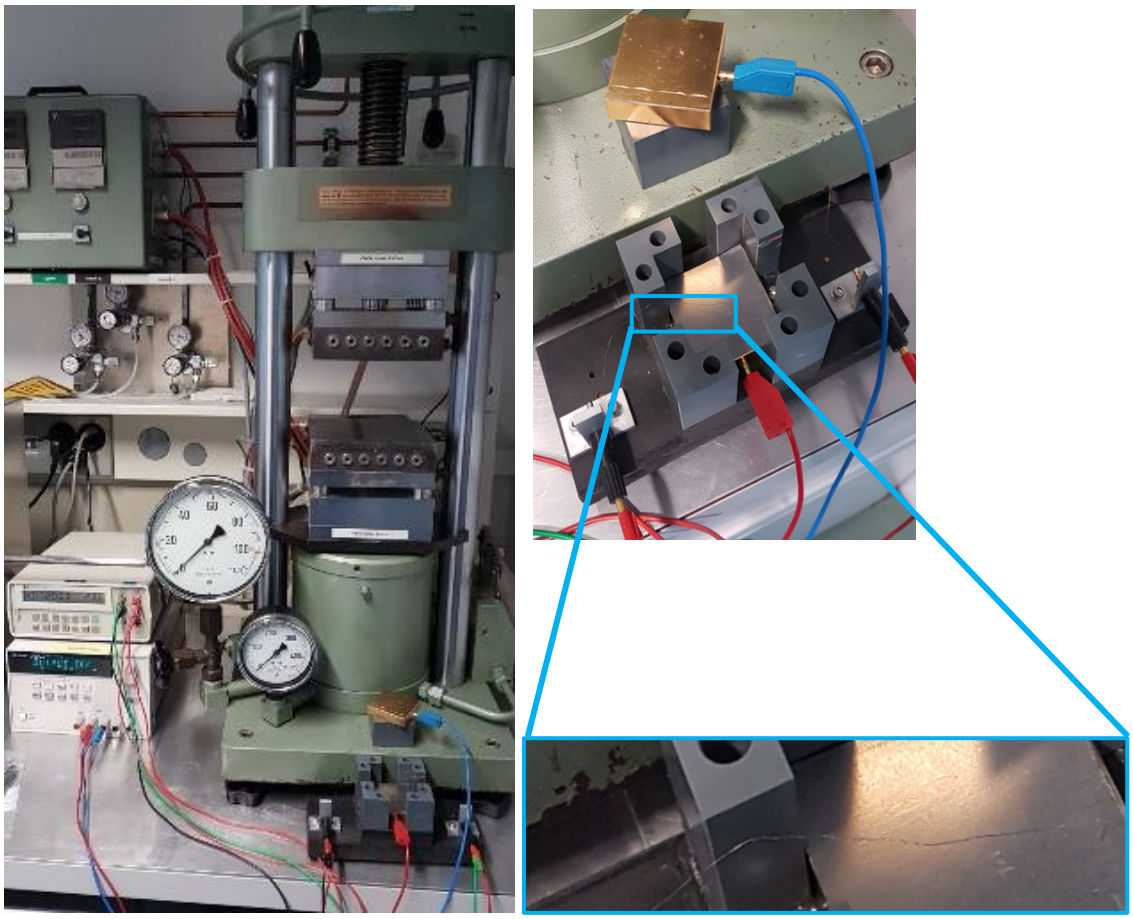

Figure 13: Through-thickness resistance measurements at PSI (left) and detail of the electrodes and the voltage wires (right).

The flexural properties were measured via 3-point bending test according to the standard DIN EN ISO 178.

The thermal conductivity in the xy-direction (in-plane) was measured via a HotDisk TPS 500S device. The dimensions of the samples were ca. 40 x 40 mm2 and their thickness varied. The sensor was placed between two identical samples and these were pressed together between styropol blocks to maximize the heat transfer (Figure 14). For all measurements a 6.4 mm sensor was used and the measuring parameters were 5 s measuring time and 300 mW applied power.

The corrosion tests were undertaken following the ex-situ corrosion test metrics from the US-DoE, but the conditions had to be adapted due to the availability of the testing equipment. The tests were performed by a GreenGT engineer at an EPFL laboratory in Sion, the Laboratory of Physical and Analytical Electrochemistry (LEPA). The working potential of the anode side of a PEMFC is close to + 0.1 V vs. NHE at an operational current density of 1 A/cm2. The target of the DoE is an anodic current at the working conditions of a PEMFC (0 to 0.1/0.2 V vs. NHE) less than 1 $\mu A/cm^2$. The potential used was 1 mV/s, instead of 0.1 mV/s, and the behavior at 0.1 mV/s was estimated from the change in corrosion current between 5 and 1 mV/s (by estimate from the log i value change). A detailed description of the method is given at the attached report.

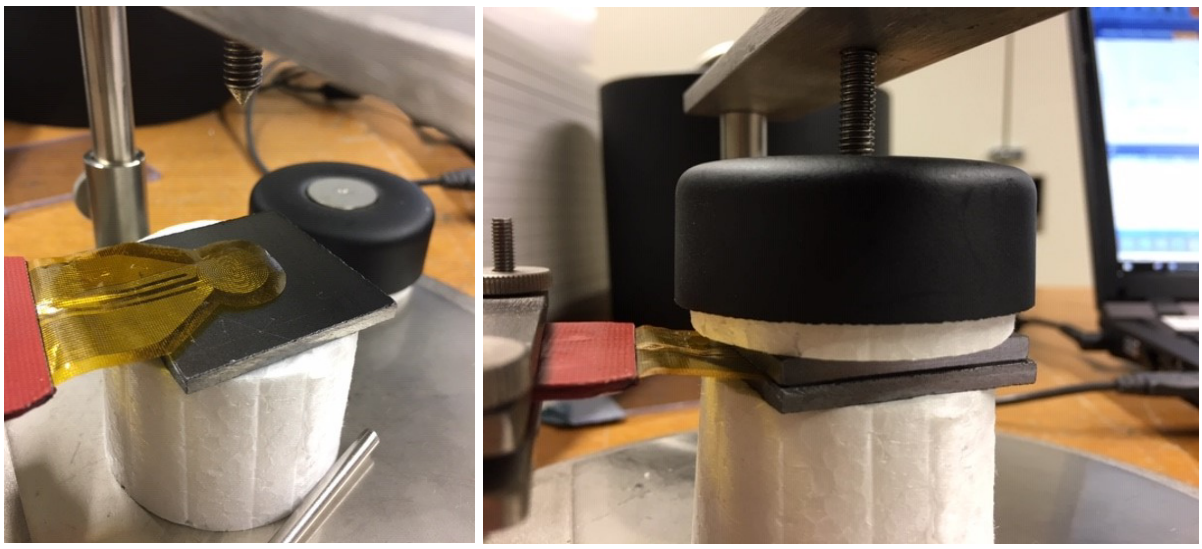

Figure 14: Sensor used (left) and measuring configuaration for in-plane thermal conductivity (right).

4 Results and Discussion

4.1 Thermoset based composites

The preparation method of the EP based compounds available at IKT did not allow the incorporation of high amount of fillers. The maximum amount was 50 wt.% which is much lower than that reported in the literature for highly conductivity thermoset compounds for BPP application [27, 29, 31, 32, 34]. Therefore the final electrical properties were below the targeted values as can been seen in Table 12.

		Electrical conductivity (S/cm)	
#		**IKT**	**PSI**
A2	50% EP, 45% Gr, 5% CB	1.6	2.4
A3	40% EP, 54% Gr, 6% CB	4.9	7.8

Table 12: Electrical conductivity values for EP based compounds.

In Table 13 the results of the anodic corrosion tests of EP based compounds are summarised. They all show good corrosion resistance but due to the low electrical conductivity they are not considered as good candidates for the specific application.

		Anodic corrosion current (A/cm^2)		
#		5 mV/s	1 mV/s	0.1 mV/s
A2	50% EP, 45% Gr, 5% CB	1.0E-04	3.2E-07	1.0E-07
A3	40% EP, 54% Gr, 6% CB	5.0E-05	6.3E-07	2.0E-07

Table 13: Results of the anodic corrosion test for EP based compounds.

4.2 Thermoplastic based composites

In order to investigate the influence of the polymeric matrix compounds with the same type and content of fillers were prepared. These consisted of 20% polymer, 40% graphite, 10% expanded graphite, 15% carbon black, 10% carbon fibers and 5% CNT. The comparison of the electrical conductivity and flexural strength values is given in Figure 15. Regarding the electrical properties, the best values are achieved with the PP and PA12 based compounds. Both polymers have a relative low melt viscosity and this facilitate a better wetting and dispersion of the fillers. PPS and LCP on the other hand showed higher flexural properties. For this project, PP was selected as the most promising matrix in order to optimize the compound formulation.

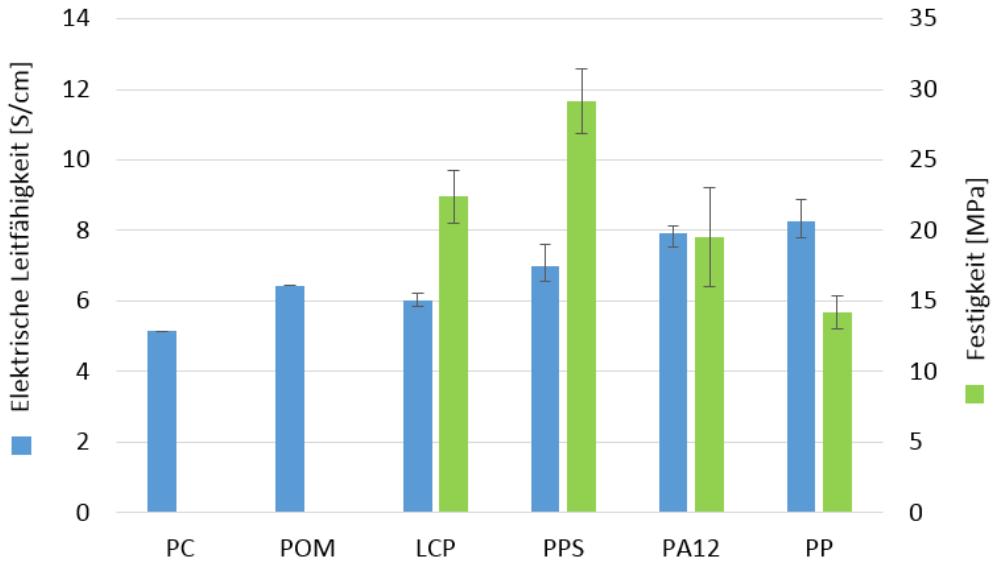

Figure 15: Influence of the polymer matrix on the electrical conductivity (blue) and the flexural strength (green) values.

The various conductive fillers were systematically tested concerning their effect on the electrical conductivity and flexural strength. Detailed information can be found at the bachelor thesis of R. Bühler which is attached to this report. Among the different graphite types shown in Table 7, Natural High-Conductive Graphite from ProGraphite provided compounds with higher conductivity and good mechanical properties. The rest of them showed similar properties. Regarding carbon black (Table 8), ENSACO 250G from Imerys resulted in higher levels of conductivity while MECHANO COND 5VP3 from H.C. Carbon gave higher flexural properties. A concentration of 15 wt% was selected as the optimum one. Expanded graphite showed better electrical properties compared to graphite while the metal fillers gave as expected the highest values of electrical conductivity.

In Table 14 the results of the anodic corrosion tests of PP based compounds are summarized. The formulations A6 and A8 can be considered as possible materials although their performance is below the target by a decade. The metal filled compounds (A1, A7 and A9) showed poor corrosion resistance and therefore are not considered as suitable fillers for the specific application.

		Anodic corrosion current (A/cm^2)		
#		5 mV/s	1 mV/s	0.1 mV/s
A1	10% PP, 47.5% Gr, 10% CB, 2.5% CNT, 30% Ag/Cu	5.0E-04	7.9E-04	1.0E-03
A6	20% PP, 60% EG, 15% CB, 5% CNT	6.3E-06	3.2E-05	1.0E-05
A7	10% PP, 47.5% Gr, 10% CB, 2.5% CNT, 30% Ag/Al	1.6E-03	6.3E-04	4.0E-04
A8	20% PP, 60% Gr, 15% CB, 5% CNT	1.0E-05	1.0E-05	1.0E-05
A9	10% PP, 47.5% Gr, 10% CB, 2.5% CNT, 30% Ag/Glass	7.9E-04	3.2E-04	1.3E-04

Table 14: Results of the anodic corrosion test for PP based compounds.

Apart from the different fillers, a coupling agent, Titanate, was incorporated to the compounds and led to a better wetting of the fillers and thus enhanced mechanical and electrical properties.

From all the compounds prepared and tested within the frame of the CompBiPol project, two optimum formulations based on the PP are selected as most promising:

Formulation #A10: 60% Gr, 15% CB, 5% CNT, 20% PP and 1.5% Titanate

Formulation #A11: 40% Gr, 20% EG, 15% CB, 5% CNT, 20% PP and 1.5% Titanate

Based on these formulations, plates of different thickness were manufactured and their electrical conductivity was measured at IKT and PSI. The values are shown in **Fehler! Verweisquelle konnte nicht gefunden werden.** and **Fehler! Verweisquelle konnte nicht gefunden werden.**. Electrical conductivity is increasing as the plate thickness increases. Higher values are measured via the PSI configuration attributed mainly to the better parallelism of the electrodes and higher applied pressure which resulted in optimum distribution of pressure and thus decreased contact resistance. The flexural properties of these formulations were characterized and a flexural strength of 19.7 MPa and 19.4 MPa was measured for #A10 and #A11, respectively. These values are very close to the US-DoE value of 25 MPa and is expected to be achieved by the optimization of the manufacturing process.

The electrical conductivity values are comparable to the highest reported for commercial available composite BPP based on thermosets and much higher compared to thermoplastic based BPPs (Figure 2, **Fehler! Verweisquelle konnte nicht gefunden werden.** and Table 3).

Comparing the values of electrical conductivity with the literature, for example the 2.65 mm thickness plate of Formulation #A10 with 41.6 S/cm is comparable to the results of Heinzel A. et al. [20] who achieved 50 S/cm for 2.5 mm thickness injection moulded plates. Similar is the comparison with the Formulation #A11, which shown a conductivity of 46.1 S/cm for 2.95 mm thickness. It is expected that injection moulding can result to a better quality of plates compared to compression moulding and this optimization step shall be included to the BPPs process development. Much higher electrical values have been reported in the literature for thermoset based compounds for BPPs [29, 31]. However, these compounds are prepared via a solvent based process which is difficult to be up-scaled for industrial production.

The thermal conductivity values of the two optimum formulations are summarized in **Fehler! Verweisquelle konnte nicht gefunden werden.** for two different plate thicknesses. The values are above the US-DoE Target (> 10 W/mK).

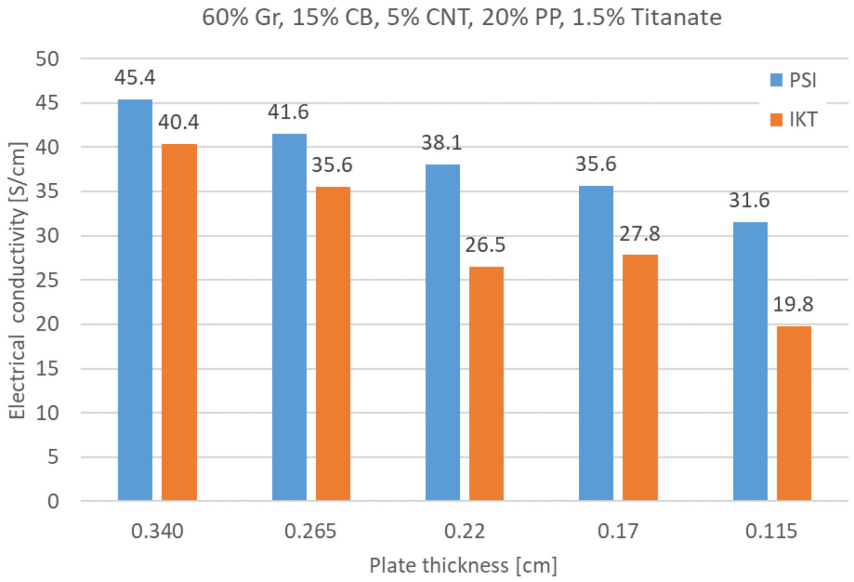

Figure 16: Effect of thickness and measurement configuration on the electrical conductivity values.

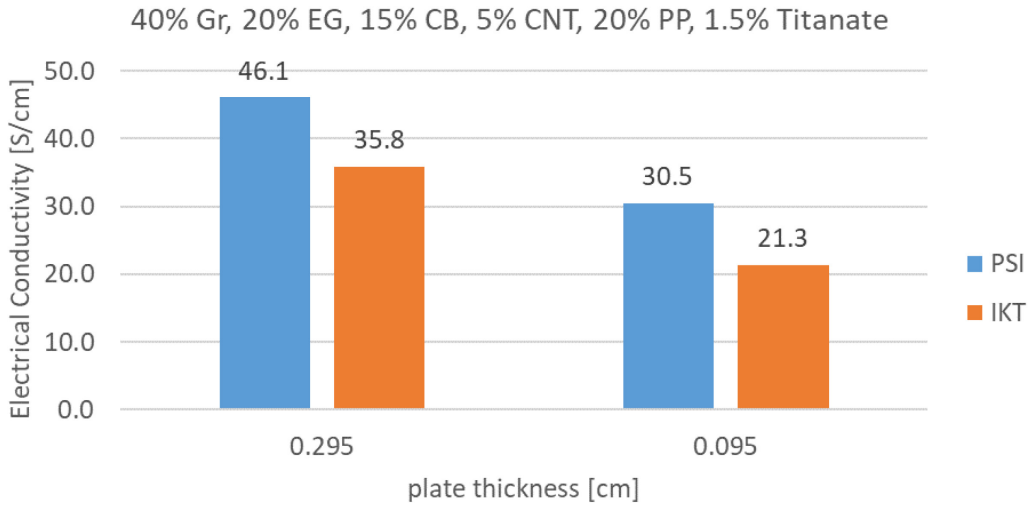

Figure 17: Effect of thickness and measurement configuration on the electrical conductivity values.

	Thickness [mm]	**Applied Power [mW]**	**Measuring Time [s]**	**In-Plane Thermal Conductivity [W/mK]**
Formulation #A10	1.5	300	5	28.5
	2.5	300	5	27.2
Formulation #A11	1	300	5	23.3
	3	300	5	23.2

Table 15: In-plane thermal conductivity.

5 Conclusions and outlook

Summarizing the above presented results, it can be concluded that CompBiPol research project resulted in promising composite compounds for the manufacturing of BPP for fuel cells. Their properties are at the same level or higher to existing thermoplastic-based BBP and composites that can be found in the literature. It is expected that these properties can be further improved with the enhancement of the mixing and pressing processes. The goal of the project has been mainly on the composite material development and no optimization of the process was foreseen within the one year duration. A continuation of this research is needed in order to fully understand the effect of the processing parameters on the electrical, thermal and mechanical properties and upscale the manufacturing process from lab to industrial-level. It is anticipated that innovative BPP plates can be in this way introduced to the market, based on the formulations developed within the CompBiPol and the new design by GREENGT.

6 Publications [within the project]

FHNW_2017 Verbundwerkstoffe für die Herstellung von Bipolarplatten, R. Bühler, Projekt 5, Fachhochschule Nordwestschweiz FHNW, 2017

FHNW_2018 Entwicklung von Polymercompounds für die Herstellung von Bipolarplatten, R. Bühler, Bachelor Thesis, Fachhochschule Nordwestschweiz FHNW, 2018

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8 Appendix

8.1 Appendix 1: Verbundwerkstoffe für die Herstellung von Bipolarplatten, R. Bühler, Projekt 5, Fachhochschule Nordwestschweiz FHNW, 2017

8.2 Appendix 2: Entwicklung von Polymercompounds für die Herstellung von Bipolarplatten, R. Bühler, Bachelor Thesis, Fachhochschule Nordwestschweiz FHNW, 2018

8.3 Appendix 3: Corrosion measurements of Composite Bipolar Plates, J.-M. Le Canut, CompBiPol Report, GreenGT, 2018